METHOD FOR DYEING ARAMID FIBERS AND DYED ARAMID FIBERS

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ABSTRACT
Methods for dyeing aramid fibers, and the dyed aramid fibers produced by these methods, which comprises a dye providing step in which a vat dye or a sulfur dye is provided to aramid fibers, a solvent treatment step in which the aramid fibers are treated by a treating solution containing a polar solvent, and after the solvent treatment step, a heat treatment step in which the aramid fibers are subjected to a heat treatment, if necessary, and having one or more dyeing operations comprising the combination of the respective steps dyeing operations. The dyeing methods can be applied to either of the para-type aramid fibers, the para-type copolymerized aramid fibers and the meta-type aramid fibers, which can be dyed to a practical color depth required for developing new applications of the aramid fibers. Colorfastness of the dyed product, in particular, colorfastness to light, is improved.
METHOD FOR DYEING ARAMID FIBERS
AND DYED ARAMID FIBERS

TECHNICAL FIELD

[0001] The present invention relates to a method for dyeing aramid fiber, in particular, to a method for dyeing which can dye the aramid fibers with a practical color depth. The present invention also relates to aramid fibers dyed by the method.

BACKGROUND ART

[0002] A wholly aromatic polyamide fiber is also called as an aramid fiber, which has high strength and high modulus of elasticity, and excellent heat resistance, dimensional stability, chemical resistance, etc., and has been used for wide uses as industrial use fibers. The aramid fibers can be roughly classified into three kinds of para-type aramid fibers (polyarylene terephthalamide fiber, etc.), para-type copolymerized aramid fibers (copolymerized fibers with polyarylene terephthalamide and 3,4'-oxydiphenyle-neterethyalthalamide), and, meta-type aramid fibers (poly- methylenes isophthalamide fibers or copolymerized fibers containing the same as a main component, etc.) depending on the position of an amide bond attached to the aromatic ring.

[0003] The para-type aramid fibers are particularly strong and excellent in modulus of elasticity, and have been widely used for protective clothes such as a bulletproof jacket, etc., friction materials such as a brake pad, etc., reinforcing materials of an optical fiber, or industrial materials such as ropes and nets which are required to have particularly high strength. In addition, the para-type copolymerized aramid fibers have been used for the similar uses as those of the para-type aramid fibers, and show their characteristics for the uses required to have chemical stability and fatigue resistance. It has been widely used, for example, for rubber reinforcing materials, ropes, and civil engineering and construction uses. On the other hand, the meta-type aramid fibers are particularly excellent in heat resistance, flame retardance, chemical resistance, etc., and have been widely used for various kinds of protective working clothes such as fire fighters' suits, etc.

[0004] These aramid fibers have rigid molecular structure and high crystallinity, and a practical color depth cannot be obtained by the same dyeing method as applied to the general fibers, and colorfastness of the obtained dyed product cannot be said to be practically sufficient. Thus, in practical, it is manufactured as dope-dyed fibers (fibers produced by adding a colorant at the stage before the spinning step) and used mainly in the meta-type aramid fibers. Such dope-dyed fibers are limited in hue, so that there is the problem that they cannot sufficiently correspond to various hues required for developing new applications of various kinds of protective working clothes or aramid fibers. Moreover, in the para-type aramid fibers or the para-type copolymerized aramid fibers, and also including the dope-dyed fibers, fibers having a practical color depth such as black and navy blue have not yet been industrially produced.

[0005] On the other hand, it has been investigated a specific dyeing method for dyeing the aramid fibers. For example, there are a high temperature and high pressure dyeing method which also uses a dyeing carrier such as benzaldehyde, acetophenone and benzyl alcohol, or a solvent dyeing method in which dyeing is carried out in a polar solvent such as N,N-dimethylformamide, dimethylsulfoxide and cyclohex-

anone at high temperature. However, these dyeing methods using a dyeing carrier or a polar solvent at high temperatures are methods mainly for dyeing meta-type aramid fibers, and they are insufficient for dyeing para-type aramid fibers or para-type copolymerized aramid fibers. Moreover, in the dyeing of the meta-type aramid fibers, when the dyeing method which uses these dyeing carriers or polar solvents at high temperature is employed, it involves the problems of causing color unevenness of the dyed product, and dimensional change or lowering in physical properties due to shrinkage, etc.

[0006] Thus, various novel dyeing methods have been investigated even now. For example, in the following Patent Document 1, it has been proposed a dyeing method in which aramid fibers are pre-treated by conc. sulfuric acid, subsequent to neutralization, injected into a dyeing bath while maintaining a predetermined moisture content without drying, and dyed by a disperse dye or a cationic dye. Also, in the following Patent Document 2, a dyeing method in which a part of vat dyes which are stable at high temperature is used, and dyeing is carried out at extremely high temperature conditions of 300 to 400° C. has been proposed.

PRIOR ART DOCUMENT

Patent Document


SUMMARY OF THE INVENTION

Problems to be Solved by the Invention

[0009] By the way, the dyeing method of the above-mentioned Patent Document 1 gives a dyed product with various hues. However, the dyeing method of the above-mentioned Patent Document 1 employs a dye such as a disperse dye and a cationic dye, etc., and there is the problem that colorfastness, in particular, colorfastness to light is bad. To the contrary, the dyeing method of the above-mentioned Patent Document 2 uses a vat dye which gives good colorfastness to light, but a dyeing temperature is an extremely high temperature whereby the dye which can be used for the method is limited, so that there is the problem that it cannot sufficiently correspond to various hues.

[0010] Also, the dyeing method of the above-mentioned Patent Document 2 involves the problems that a specific device is required and a cost for energy becomes large. Moreover, the dyeing method of the above-mentioned Patent Document 2 is not yet sufficient to dye the para-type aramid fibers or the para-type copolymerized aramid fibers with a practical color depth. On the other hand, when the dyeing method of the above-mentioned Patent Document 2 is applied to the meta-type aramid fibers, the fibers are treated at a temperature markedly higher than the glass transition temperature thereof, so that there is the problem that the physical properties of the fibers are markedly lowered.

[0011] Thus, the present invention has been done in view of the above mentioned problems, and an object thereof is to provide a method for dyeing aramid fibers and dyed aramid fibers, which method is a dyeing method which can be applied to either of the para-type aramid fibers, the para-type copolymerized aramid fibers and the meta-type aramid fibers, which can be dyed to a practical color depth required for developing new applications of the aramid fibers, and color
unevenness, dimensional change, or lowering in physical properties are not generated so remarkably in the aramid fibers after dyeing. Further, colorfastness of the dyed product, in particular, colorfastness to light is good.

Means to Solve the Problems

To solve the above-mentioned problems, the present inventors have intensively studied, and as a result, they have found that the above-mentioned problems can be solved by employing a vat dye or a sulfur dye which has good colorfastness to light for dyeing aramid fibers, and using a step of providing these dyes onto the aramid fibers, and a step of treating the aramid fibers with a polar solvent in combination, whereby the present invention has been accomplished.

That is, a method for dyeing aramid fibers according to the present invention comprises, according to the definition of claim 1, a dye providing step in which a vat dye or a sulfur dye is provided to aramid fibers, a solvent treatment step in which the aramid fibers are treated by a treating solution containing a polar solvent, and after the solvent treatment step, a heat treatment step in which the aramid fibers are subjected to a heat treatment, if necessary, and having at least one dyeing operation among the following four dyeing operations,
dyeing operation 1: dyeing providing step → solvent treatment step,
dyeing operation 2: solvent treatment step → dyeing providing step,
dyeing operation 3: dyeing providing step → solvent treatment step → heat treatment step,
dyeing operation 4: solvent treatment step → heat treatment step → dyeing providing step, once or more.

Also, the present invention is, according to the definition of claim 2, in the method for dyeing aramid fibers according to claim 1, wherein the polar solvent has a value of a solubility parameter (δ) within a range of 18 to 32 (MPa)^1/2.

Further, the present invention is, according to the definition of claim 3, in the method for dyeing aramid fibers according to claim 1, wherein the polar solvent is at least one selected from the group consisting of N-methylpyrrolidone, N,N-dimethylformamide, N,N-dimethylacetamide, dimethylsulfoxide, benzyl alcohol, diethylene glycol, triethylene glycol, sulfuric acid, formic acid, lactic acid and oxalic acid.

Moreover, a method for dyeing aramid fibers according to the present invention comprises, according to the definition of claim 4, the method for dyeing aramid fibers according to any one of claims 1 to 3, and a pre-dyeing step which is carried out before the method for dyeing or a post-dyeing step which is carried out after the same, wherein the aramid fibers are dyed by a dye other than the vat dye or the sulfur dye in the pre-dyeing step or in the post-dyeing step.

Furthermore, dyed aramid fibers according to the present invention comprise, according to the definition of claim 5, dyed by the method for dyeing aramid fibers according to any one of claims 1 to 3.

In addition, the present invention is, according to the definition of claim 6, in the dyed aramid fibers according to claim 5, lightness (L* value) in an L*a*b* colorimetric system is 38 or less.

Also, the present invention is, according to the definition of claim 7, in the dyed aramid fibers according to claim 5, wherein lightness (L* value) in an L*a*b* colorimetric system is 30 or less.

Further, the dyed aramid fibers according to the present invention comprise, according to the definition of claim 8, fibers dyed by the method for dyeing aramid fibers according to claim 4.

Moreover, the present invention is, according to the definition of claim 9, in the dyed aramid fibers according to claim 8, wherein lightness (L* value) in an L*a*b* colorimetric system is 30 or less.

Effects of the Invention

According to the present invention, the method can be applied to either of the para-type aramid fibers, the para-type copolymerized aramid fibers or the meta-type aramid fibers, and can dye these aramid fibers with a practical color depth. Also, according to the present invention, color unevenness or dimensional change, or lowering in physical properties is not markedly generated in the aramid fibers after the dyeing. Moreover, since a vat dye or a sulfur dye having good colorfastness, in particular, colorfastness to light is used, colorfastness, in particular, colorfastness to light of the dyed aramid fibers becomes good.

In addition, by changing a used concentration and hue of the vat dye or the sulfur dye to be used, a dyed product from a pale color to a dark color with various hues can be obtained. In particular, according to the present invention, the para-type aramid fibers or the para-type copolymerized aramid fibers can be dyed with a very dark color such as black and navy blue which had been deemed to be difficult.

Here, as one of the methods to evaluate a dark color such as black and navy blue, there is lightness (L* value) in a L*a*b* colorimetric system which had been standardized by International Commission on Illumination (CIE) in 1976, and in Japan, it had been adopted in JIS Z8729. This L* value is shown in the range of 100 (white) to 0 (black), and a smaller L* value can be evaluated to be a dark color.

For example, in the dope-dyed fibers of the commercially available meta-type aramid fibers or para-type copolymerized aramid fibers, it has been obtained an L* value of 25 to 27 in the very dark color such as black and navy blue. Accordingly, in the present invention, the L* value of 38 or less can be judged as a dark color; and further, the L* value of 30 or less can be judged as a very dark color. In the present invention, not only the meta-type aramid fibers but also the para-type aramid fibers or the para-type copolymerized aramid fibers can be dyed to a dark color or a very dark color not by the spun-dyeing method but by the dyeing method.

Also, as a step before or after the method for dyeing aramid fibers according to the present invention, a pre-dyeing step or a post-dyeing step by a dye other than the vat dye and the sulfur dye can be carried out. By carrying out these dyeing steps, fuzz at the surface of the aramid fibers themselves is more sufficiently dyed, so that dyeing quality and color depth are further improved. On the other hand, when the aramid fibers are mixed with the other chemical fibers or natural fibers to form a mixed fiber, hue of the aramid fibers and that of the other fibers can be unified by subjecting to these dyeing steps, whereby the dyeing quality and the color depth of the dyed product are further improved.

Thus, according to the present invention, a method for dyeing aramid fibers and dyed aramid fibers having good colorfastness, in particular, colorfastness to light of the dyed product, abundant in hue and a practical color depth can be provided. This is effective for developing novel use of the aramid fibers.
EMBODIMENTS TO CARRY OUT THE INVENTION

[0028] In the aramid fibers to be dyed by the dyeing method according to the present invention, for example, as the para-type aramid fibers, there may be mentioned Twaron (Registered Trademark) available from Teijin Limited, and Kevlar (Registered Trademark) available from Du Pont Kabushiki Kaisha, and as the para-type copolymerized aramid fibers, there may be mentioned Technora (Registered Trademark) available from Teijin Limited. On the other hand, as the meta-type aramid fibers, there may be mentioned Conex (Registered Trademark) available from Teijin Limited, and Nomex (Registered Trademark) available from Du Pont Kabushiki Kaisha.

[0029] In the present invention, the aramid fibers may be any form, and may be in the state of fibers such as filament fibers, staple fibers, etc., or in the state of a fiber structure such as filament yarn, spun yarn, fabrics, knit fabrics, non-woven fabrics, rope, a net, etc. Also, it may be either one of the para-type aramid fibers, the para-type copolymerized aramid fibers or the meta-type aramid fibers, or in the state of mixed fibers thereof. Moreover, it may be in the state of mixed fibers of the aramid fibers and the other chemical fibers or natural fibers.

[0030] In the present invention, the aramid fibers are dyed by a vat dye or a sulfur dye. These vat dyes or sulfur dyes are each dyes having good colorfastness, in particular, excellent in colorfastness to light.

[0031] Here, the vat dye is generally used for dyeing of cotton, etc., and is a dye essentially insoluble in water, but it is reduced by a reducing agent such as sodium dithionite, etc., to adsorb to the fibers in the form of leuco acid or leuco salt, and thereafter, is oxidized and dyeing to the fibers as a dye insoluble in water again.

[0032] On the other hand, the sulfur dye is a dye containing a sulfur atom in the molecule, and is generally used for dyeing of cotton, etc. This sulfur dye is also a dye essentially insoluble in water, but it is reduced by a reducing agent such as sodium sulfite, etc., to become water-soluble to adsorb to the fibers, and thereafter, is oxidized and dyeing to the fibers as a dye insoluble in water again.

[0033] However, in the present invention, the vat dye or the sulfur dye is used without reduction and dyed to the aramid fibers in the state of a dye insoluble in water. The vat dye or the sulfur dye does not have potent affinity as it were, which can dye to the aramid fibers as such. Also, when the vat dye or the sulfur dye is reduced to make it water-soluble, affinity to the aramid fibers is further lowered.

[0034] In the present invention, however, by employing a solvent treatment of the aramid fibers using a polar solvent in combination, it can be considered that dyeing property of the vat dye or the sulfur dye to the aramid fibers would be revealed. Further, when a heat treatment is carried out, if necessary, after the solvent treatment, dyeing property of the vat dye or the sulfur dye to the aramid fibers is improved in some cases. However, at the present stage, it is not yet clear about the dyeing mechanism of the vat dye or the sulfur dye to the aramid fibers according to the present invention.

[0035] In the following, the method for dyeing aramid fibers according to the present invention will be explained based on the respective embodiments.

(1) First Embodiment

[0036] The dyeing method according to the first embodiment comprises a dye providing step in which a vat dye or a sulfur dye is provided to the aramid fibers, and a solvent treatment step in which the aramid fibers are treated by a treating solution containing a polar solvent. The order of these dye providing step and solvent treatment step is not particularly limited, and it is preferred to carry out the solvent treatment step after the dye providing step. In this first embodiment, the dye providing step in which the vat dye or the sulfur dye is provided to the aramid fibers in a non-reduced state is firstly carried out, subsequently the solvent treatment step in which the aramid fibers to which the vat dye or the sulfur dye had been provided are treated by a treating solution containing a polar solvent is carried out.

[0037] In this first embodiment, these series of steps are generically called as “dyeing operation 1”. Incidentally, this dyeing operation 1 (dye providing step→solvent treatment step) may be carried out only once, or may be repeated a plural number of times, depending on necessity. By repeating this dyeing operation a plural number of times, aramid fibers with a denser color can be obtained.

A. Dye Providing Step

[0038] The vat dye to be used in the dye providing step may be mentioned a dye generally used for dyeing of cotton, etc. Also, in the present invention, it is preferred to use a super fine dye having an average dispersed particle diameter in the state of dispersing in a dyeing solution of several μm or less, more preferably 1 μm or less. In addition, among these vat dyes, it is more preferred to use, in particular, each dye of C.I. Vat Yellow 33, C.I. Vat Brown 1, C.I. Vat Red 1, C.I. Vat Violet 9, C.I. Vat Blue 4, C.I. Vat Blue 6, C.I. Vat Blue 20, C.I. Vat Green 1, C.I. Vat Green 3, C.I. Vat Black 8, C.I. Vat Black 25, etc.

[0039] On the other hand, the sulfur dye to be used in the dye providing step may be mentioned a dye generally used for dyeing of cotton, etc. Also, among these sulfur dyes, it is more preferred to use, in particular, each dye of C.I. Sulphur Yellow 16, C.I. Sulphur Orange 1, C.I. Sulphur Red 6, C.I. Sulphur Blue 7, C.I. Sulphur Blue 15, C.I. Sulphur Black 11, etc.

[0040] At the stage of providing a dye to the aramid fibers, the vat dye or the sulfur dye is not in a reduced state, and is a dye insoluble in water. Accordingly, for providing a dye to the aramid fibers in the dye providing step, a dyeing solution in which the vat dye or the sulfur dye is dispersed in water is used. In this dyeing solution, the vat dye or the sulfur dye is contained in a non-reduced dispersed state, and, if necessary, a migration preventive agent may be used therein in combination. For providing the dyeing solution, any methods may be employed, and may be simple dipping, dipping and squeezing liquid, or may be provision by spray, ink jet, etc.

[0041] The aramid fibers to which the dyeing solution had been provided are dried thereafter, if necessary. Drying of the aramid fibers may be carried out at any temperatures, and generally dried at a temperature of about 80°C. to 120°C. In addition, after drying the aramid fibers, a heat treatment (which is different from the heat treatment step mentioned below) may be further carried out at high temperature. Or else, the aramid fibers to which the dyeing solution had been provided may be subjected to a heat treatment at a temperature of about 120°C. to 200°C., or a higher temperature than the above, which also acts as drying procedure.
If the drying temperature is lower than 80°C, a longer time is required for drying the aramid fibers. On the other hand, if the treatment temperature is higher than 200°C, in particular, it is higher than 280°C, lowering in physical properties of the aramid fibers occurs remarkably in some cases. In particular, in the case of the meta-type aramid fibers, a heat treatment at a temperature exceeding its glass transition temperature causes lowering in physical properties. In addition, it is treated at an extremely high temperature, the vat dye or the sulfur dye decomposes in some cases whereby hue is markedly changed.

On the other hand, the drying time may be optionally selected depending on a kind or a form of the aramid fibers, and a drying temperature, and is not a particular problem. The drying time is generally a time of about 30 seconds to 30 minutes. For example, when the aramid fibers are fabrics, the drying time is preferably about 1 minute to 10 minutes when the drying temperature is 105°C.

At the stage where the drying has finished, the vat dye or the sulfur dye is in the state that they are uniformly provided onto the aramid fibers. However, the aramid fibers are not in the state that they are completely dyed by the vat dye or the sulfur dye. However, at this stage, the vat dye or the sulfur dye is attached to the aramid fibers with a certain degree of affinity, whereas it is not yet reached to dyeing. Here, the reason why the vat dye or the sulfur dye is attached to the aramid fibers is not clear, but it can be considered that these dyes are attached onto the surface of the aramid fibers by physical action such as an intermolecular force in an unreduced water-insoluble state.

Here, when the aramid fibers are a fabric state, a series of the treatments can be carried out by running the fabrics to the longitudinal direction. In this case, the running aramid fiber fabrics are firstly dipped in a bath in which a dyeing solution has been filled. Subsequently, an excess dyeing solution is squeezed from the aramid fiber fabrics by a squeezing means such as mangle, etc. According to these procedures, aramid fiber fabrics to which a predetermined amount of the dyeing solution has been provided are obtained. Next, the aramid fiber fabrics after squeezing is introduced in a heat treatment device such as a pin tenter while running and dried therein.

### B. Solvent Treatment Step

The aramid fibers after the dye providing step are injected into the subsequent solvent treatment step without washing. In the solvent treatment step, the aramid fibers are treated by a polar solvent. In the present invention, the polar solvent is widely interpreted, and is to be called a substance having a polar functional group in the molecular structure of a solvent. For example, among the polar solvents, an aprotic polar solvent may be mentioned N-methylpyrrolidone, N,N-dimethylformamide, N,N-dimethylacetamide, dimethylsulfoxide, acetonophenone, methyl ethyl ketone, N-butylphthalimide, N-isopropylphthalimide, N,N-dimethylformamide, etc. These aprotic polar solvents may be used alone, or in combination of two or more, or may be used by formulating with the following mentioned protonic polar solvent(s). Among these aprotic polar solvents, as a solvent which difficulty causes shrinkage or lowering in physical properties of the aramid fibers, and particularly effective for dyeing the vat dye or the sulfur dye, N-methylpyrrolidone, N,N-dimethylformamide, N,N-dimethylacetamide and dimethylsulfoxide are preferably mentioned.

Also, among the polar solvents, the protonic polar solvent may be mentioned protonic acids such as sulfuric acid, formic acid, lactic acid, maleic acid, oxalic acid, etc.; alcohols such as 1-propanol, 1-octanol, benzyl alcohol, DL-β-ethylphenethyl alcohol, 2-ethoxybenzyl alcohol, 3-chlorobenzyl alcohol, 2,5-dimethylbenzyl alcohol, 2-nitrobenzyl alcohol, p-isopropylbenzyl alcohol, 2-methylphenethyl alcohol, 3-methylphenethyl alcohol, 4-methylphenethyl alcohol, 2-methoxybenzyl alcohol, 3-isobenzyl benzyl alcohol, cinnamic alcohol, p-anisyl alcohol, benzhydrol, 2-(4-chlorophenoxy) ethanol, 2-(4-chlorophenoxy)ethanol, etc.; glycols such as ethylene glycol, diethylene glycol, triethylene glycol, PEG200, PEG400, PEG600, propylene glycol, polypropylene glycol, etc., and further a monoether or monoester of the glycol such as ethylene glycol monomethyl ether, diethylene glycol monomethyl ether, ethylene glycol monoethyl ether, ethylene glycol monobenzyl ether, propylene glycol monomethyl ether, diethylene glycol monobenzyl ether, propylene glycol monoethyl ether, propylene glycol monobenzyl ether, propylene glycol monomethyl ether, polypropylene glycol monomethyl ether, propylene glycol monobenzyl ether, polypropylene glycol monomethyl ether, polypropylene glycol monobenzyl ether, ethylene glycol monophenyl ether, propylene glycol monophenyl ether, diethylene glycol monophenyl ether, cellulose, n-butyl cellosolve, hydroxyethyl acrylate, etc. These protonic polar solvents may be used alone, or in combination of two or more, or may be used by formulating with the above-mentioned aprotic polar solvent(s). Among these protonic polar solvents, as a solvent which difficulty causes shrinkage or lowering in physical properties of the aramid fibers, and particularly effective for dyeing the vat dye or the sulfur dye, benzyl alcohol, diethylene glycol, triethylene glycol, sulfuric acid, formic acid, lactic acid and oxalic acid are preferably mentioned.

Also, as a quantitative index which shows polarity of the polar solvent used in the present invention, a solubility parameter (δ) can be used. In the present invention, it is preferred to use a polar solvent having a value of the solubility parameter within the range of δ=-18 to 32 (MPa)^{1/2}. Moreover, it is more preferred to use a polar solvent having a value of the solubility parameter within the range of δ=-19 to 28 (MPa)^{1/2}. Here, for example, the value of the solubility parameter of the para-type aramid fibers is to be made δ=23 (MPa)^{1/2} (J. E. Mark, Physical Properties of Polymers Handbook, New York: Woodbury, 1986). Accordingly, it seems that an action of the polar solvent to the aramid fibers is caused by the fact that the value of the solubility parameter of the polar solvent is within the above-mentioned range, which is close to the value of the solubility parameter of the aramid fibers. According to the fact, dyeing property of the vat dye or the sulfur dye to the aramid fibers is improved, whereby aramid fibers having a more practical color depth can be obtained.

These polar solvents may be used alone or may be used by mixing two or more solvents as mentioned above. Also, a concentration of the polar solvent to be used in the solvent treatment may be optionally selected depending on a kind or a shape of the aramid fibers to be treated, and a treatment temperature, and in general, it is preferred to contain 40% by weight to 100% by weight, and more preferably to contain 50% by weight to 100% by weight. Please be noted that oxalic acid is a solid generally having crystal water, and its solubility is a little. Thus, as far as the oxalic acid is concerned, it is preferred to use as an aqueous solution of about 10% by weight.

On the other hand, with regard to sulfuric acid to be used in the manufacturing step of the para-type aramid fibers,
it is necessary to set the concentration to be used to narrower. In this solvent treatment step, it is preferred to use an aqueous sulfuric acid solution with a concentration of 70% by weight to 90% by weight. Moreover, it is further preferred to use an aqueous sulfuric acid solution with a concentration of 75% by weight to 85% by weight.

[0051] Also, when the aramid fibers mainly comprise the meta-type aramid fibers, it is more preferred to use an aqueous sulfuric acid solution with a concentration of 75% by weight to 80% by weight.

[0052] When the concentration of the polar solvent is within the above-mentioned range, the color depth becomes within a relatively stable range, and even if the concentration of the polar solvent is slightly fluctuated, the color depth is not so remarkably changed. Accordingly, stable industrial production can be done when the concentration of the polar solvent is within the above-mentioned range.

[0053] Here, a diluent of the polar solvent may be used any material so long as it has compatibility with the polar solvent to be used, and water is generally used. In the case of a certain kind of the polar solvent, for example, N-methylpyrrolidone, etc., by mixing a certain amount of water, a denser dyed product can be obtained. On the other hand, if the concentration of the polar solvent is lower than the above-mentioned range, and an amount of water in the solvent treatment solution is increased, it is not preferred since the vat dye or the sulfur dye attached to the aramid fibers in the dye providing step drop into the solvent treatment solution in some cases.

[0054] A treatment temperature of the polar solvent may be optionally selected depending on a kind or a shape of the aramid fibers to be treated, and a treatment time, and it is generally treated at a temperature of 0°C to 70°C. In addition, it is preferably a temperature of 10°C to 60°C. When sulfuric acid is used, the temperature of the aqueous sulfuric acid solution may be a temperature of 0°C or higher and 50°C or lower, and more preferably at a temperature of 0°C or higher and 30°C or lower.

[0055] When the temperature of the polar solvent is within the above-mentioned range, the color depth is within the relatively stable range, and even if the temperature of the polar solvent is slightly fluctuated, the color depth does not so remarkably change. Accordingly, stable industrial production can be done when the temperature of the polar solvent is within the above-mentioned range. On the other hand, if the temperature of the polar solvent is higher than the above-mentioned range, lowering in physical properties or extreme shrinkage of the aramid fibers sometimes occurs. Also, by slightly varying the temperature of the polar solvent, the color depth sometimes markedly changes. It is thought that a high temperature polar solvent causes marked change in molecular structure of the aramid fibers.

[0056] Also, a treatment time of the solvent treatment may be optionally selected depending on a concentration and a temperature of the polar solvent, and it is generally treated with a time of about 0.1 seconds to 30 minutes. Further, the treatment time of the solvent treatment is preferably about 1 second to 5 minutes. Even if the treatment time of the solvent treatment is about 0.1 seconds, the effects of the solvent treatment can be maintained. Thus, when the treatment time of the solvent treatment is about 0.1 seconds to 30 minutes, even if the treatment time is slightly fluctuated, the color depth is not so remarkably changed, and the fibers can be dyed with a practical color depth.

[0057] Thus, the treatment time of the solvent treatment is preferably controlled within the predetermined range. Accordingly, the aramid fibers treated by the polar solvent are preferably washed quickly. Also, when the treatment is carried out by sulfuric acid, the fibers are preferably neutralized and washed quickly. Here, washing of the aramid fibers may be carried out by washing with water or washing with hot water, and for the purpose of removing the vat dye or the sulfur dye which is attached onto the surface of the aramid fibers with undying state, reduction washing may be carried out.

[0058] Here, when the aramid fibers are a fabric state, the solvent treatment can be carried out by running to the longitudinal direction. In this case, the running aramid fiber fabrics are firstly immersed into a bath filled with a treating solution containing a polar solvent. Subsequently, an excess treating solution is squeezed from the aramid fiber fabrics by a squeezing means such as mangle, etc. Next, the aramid fiber fabrics after the squeezing are introduced in a continuous washing device while it is running, and are subjected to washing, neutralization washing or reduction washing. When these series of the treatments are carried out continuously, the time from immersion to washing, neutralization washing or reduction washing can be controlled stably. Accordingly, to the above, the treatment time of the immersing treatment can be maintained at a preferred timing and a uniform solvent treatment can be carried out.

[0059] Incidentally, it is not clear about the action of these solvent treatments, but it can be thought that, by treating the aramid fibers with the polar solvent having a concentration as mentioned above, intermolecular bonds of the aramid fibers having a rigid molecular structure and high crystallinity are partially relaxed to form many fine voids. On the other hand, it can be also thought that these polar solvents set on the dye molecules. According to the above, the vat dye or the sulfur dye attached onto the surface of the fibers by the dye providing step is thought to be firmly dyed to the fine voids of the aramid fibers by the solvent treatment step.

[0060] In this first embodiment, the vat dye or the sulfur dye having particularly good colorfastness to light is used as mentioned above. According to the above, by carrying out these series of the dyeing operation 1 (dye providing step→solvent treatment step), a dyed product of the aramid fibers having a practical color depth, and having good colorfastness, particularly good colorfastness to light can be obtained. In particular, the dyeing method according to the present invention is a specific dyeing method which has never been used in the conventional dyeing methods, and it never uses the means of adsorption by reduction which is the inherent dyeing mechanism of the vat dye or the sulfur dye.

[0061] Also, by repeating the above-mentioned dyeing operation 1 (dye providing step→solvent treatment step) a plural number of times, the color depth of the aramid fibers can be improved. That is, to the aramid fibers dyed by the dyeing operation 1 once according to the above-mentioned method, a second time dyeing operation 1 is again carried out, aramid fibers with a denser color can be obtained. Further, the same dyeing operation 1 is repeated again, the color depth can be more improved. According to the above, colorfastness of the dyed product dyed to a dense color can be maintained with a good state.
(2) Second Embodiment

[0062] The dyeing method according to this second embodiment comprises a dye providing step in which the vat dye or the sulfur dye is provided to the aramid fibers, a solvent treatment step in which the aramid fibers are treated by a treating solution containing a polar solvent, and a heat treatment step in which the aramid fibers after the solvent treatment step are subjected to the heat treatment. In this second embodiment, these series of the steps are generically called to as “dyeing operation 3”. Incidentally, the dyeing operation 3 (dye providing step→solvent treatment step→heat treatment step) may be carried out only once, or may be repeated a plural number of times, depending on necessity. By repeating this dyeing operation a plural number of times, aramid fibers with a denser color can be obtained.

A. Dye Providing Step

[0063] The dye providing step in this second embodiment is carried out the same operations as those of the dye providing step in the above-mentioned first embodiment.

B. Solvent Treatment Step

[0064] The solvent treatment step in this second embodiment is carried out by the same operations as those of the solvent treatment step in the above-mentioned first embodiment. Incidentally, in this second embodiment, the aramid fibers after the solvent treatment is introduced into the subsequent heat treatment step without carrying out the washing, neutralization washing or reduction washing.

C. Heat Treatment Step

[0065] After the above-mentioned solvent treatment step, the aramid fibers have already been dyed by the vat dye or the sulfur dye. Here, by carrying out the heat treatment, it can be thought that dyeing of the vat dye or the sulfur dye to the aramid fibers is more progressed so that the dyed product becomes more firm. However, if sulfuric acid is used as a polar solvent, fiber strength is markedly lowered so that the heat treatment cannot be carried out.

[0066] The heat treatment may be a dry heat treatment or a wet heat treatment, and the dry heat treatment is generally preferred. The heat treatment is preferably carried out at a temperature of 50°C or higher and 200°C or lower. In the heat treatment step, the aramid fibers are treated in the state where the polar solvent is attached thereto, so if it is higher than 200°C, lowering in physical properties of the aramid fibers is considered to be caused so that it is not preferred. Also, if it is treated at an extremely high temperature, the vat dye or the sulfur dye is sometimes decomposed and hue is markedly changed.

[0067] On the other hand, the treatment time of the heat treatment may be optionally selected depending on a kind or a form of the aramid fibers, and a kind of the vat dye or the sulfur dye to be used, and it does not become a particular problem and is generally carried out with a time of about 30 seconds to 30 minutes. Further, the treatment time of the heat treatment is preferably a time of about 30 seconds to 5 minutes. Even if the treatment time of the heat treatment is a time of about 30 seconds, the effects of the heat treatment can be maintained. Thus, if the treatment time of the heat treatment is a time of about 30 seconds to 30 minutes, even when the treatment time is slightly fluctuated, the color depth is not so remarkably changed and the fibers can be dyed with a practical color depth.

[0068] Here, when the aramid fibers are a fabric state, the aramid fiber fabrics after the above-mentioned solvent treatment step may be introduced into a continuous heat treatment device while running the same to carry out the heat treatment.

When the series of the treatments from the above-mentioned solvent treatment step to the heat treatment step is carried out continuously, the treatment time from immersing in the solvent to the heat treatment can be controlled stably, the treatment times of the solvent treatment and the heat treatment can be maintained to a preferred timing, and uniform solvent treatment and heat treatment can be carried out.

[0069] Here, it is not clear about the action on the solvent treatment and the heat treatment in combination, but it can be thought that, by treating the aramid fibers with the polar solvent having a concentration as mentioned above, intermolecular bonds of the aramid fibers having a rigid molecular structure and high crystallinity are partially relaxed to form many fine voids. On the other hand, it can be also thought that the action of the polar solvent on the dye molecules is increased by the heat treatment.

[0070] According to the above, the vat dye or the sulfur dye attached onto the aramid fibers by the solvent treatment step is thought to be firmly dyed to the fine voids of the aramid fibers by the heat treatment step after the solvent treatment step.

[0071] Next, the aramid fibers after the heat treatment step are washed to remove the remaining polar solvent. The washing may be carried out washing with water or washing with hot water, and for the purpose of removing the vat dye or the sulfur dye which is attached onto the surface of the aramid fibers with undying state, reduction washing may be carried out.

[0072] In this second embodiment, as mentioned above, the vat dye or the sulfur dye which has particularly good colorfastness to light is used. According to the above, by carrying out these series of dyeing operation 3 (dye providing step→solvent treatment step→heat treatment step), a dyed product of the aramid fibers having a practical color depth, and having good colorfastness, particularly good colorfastness to light can be obtained. In particular, the dyeing method according to the present invention is a specific dyeing method which has never been in the conventional dyeing methods, and it never uses the means of adsorption by reduction which is the inherent dyeing mechanism of the vat dye or the sulfur dye.

[0073] Also, by repeating the above-mentioned dyeing operation 3 (dye providing step→solvent treatment step→heat treatment step) a plural number of times, the color depth of the aramid fibers can be improved. That is, to the aramid fibers dyed by the dyeing operation 3 once according to the above-mentioned method, a second time dyeing operation 3 is again carried out, aramid fibers with a denser color can be obtained. Further, the same dyeing operation 3 is repeated again, the color depth can be more improved. According to the above, colorfastness of the dyed product dyed to a dense color can be maintained with a good state.

(3) Third Embodiment

[0074] The dyeing method according to this third embodiment has a pre-dyeing step which dyes the aramid fibers with a dye other than the vat dye and the sulfur dye before the
dyeing operation 1 or the dyeing operation 3 explained in the above-mentioned first embodiment or the above-mentioned second embodiment. Incidentally, the above-mentioned dyeing operation 1 or the dyeing operation 3 carried out after the pre-dyeing step may be carried out once alone, or may be repeated a plural number of times, depending on necessity. By repeating the dyeing operation 1 or the dyeing operation 3 a plural number of times, aramid fibers with a denser color can be obtained.

D1. Pre-Dyeing Step

[0075] In the dyeing method according to this third embodiment, a pre-dyeing step is firstly carried out to the undyed aramid fibers. In this pre-dyeing step, a dyeing solution containing a dye other than the vat dye and the sulfur dye is used. The dyeing method of the pre-dyeing step may be any method, dyeing mainly by dip dyeing is carried out. A prescription of the dyeing solution to be used in the pre-dyeing step may be the same as that of the dye to be used in the ordinary dyeing method. Accordingly, when the aramid fibers themselves are dyed, in the same manner as in the conventional dyeing method of the aramid fibers, a dyeing carrier, etc., may be used in combination. On the other hand, when the aramid fibers are mixed with the other chemical fibers or natural fibers to form a mixed fiber, and the other fibers are to be dyed, the ordinary dyeing method to the other fibers may be carried out.

[0076] When the aramid fibers themselves are to be dyed in the pre-dyeing step, any dyes may be used as a dye to be used so long as it is a dye having an affinity to the aramid fibers. For example, a disperse dye, a cationic dye or an acid dye, etc., may be preferably used similarly as in the dyeing of the usual polamid fibers. In particular, it is preferred to use a dye which has been selected as a dye for the aramid fibers in points of dyeing property and colorfastness. On the other hand, when the aramid fibers are mixed with the other chemical fibers or natural fibers to form a mixed fiber, and the other fibers are to be dyed, a dye suitable for the other fibers may be used. For example, when the other fibers are polyester fibers, a disperse dye is to be used. In addition, when the other fibers are cotton or rayon fibers, a reactive dye or a direct dye, etc., may be used.

[0077] When the aramid fibers themselves are to be dyed, the procedure can be carried out so that the aramid fibers are thrown into a dyeing solution containing a dye, a temperature of the dyeing solution is raised to a dyeing temperature, and the dyeing temperature is maintained at a predetermined time. The dyeing temperature may be adjusted depending on a kind or a form of the aramid fibers, and, a kind and a color depth of the dye to be used, and it may be generally a temperature of 80° C. to 150° C. Also, the temperature is preferably 100° C. to 140° C., and more preferably the temperature is 120° C. to 135° C. If the temperature exceeds 100° C. in the dyeing, high temperature and high pressure dyeing machine is used.

[0078] When the aramid fibers themselves are to be dyed, if the dyeing temperature is lower than 80° C., sufficient color depth cannot be obtained, on the other hand, if the dyeing temperature is higher than 150° C., it requires a device with a specific specification as compared with the high temperature and high pressure dyeing machine generally used, and an energy cost is large.

[0079] On the other hand, the dyeing time after temperature raising may be optionally selected depending on a kind of the dye, and a relation between the dyeing temperature and the dyeing device and, for example, at a dyeing temperature of 135° C. using a disperse dye, it is preferably within the range of 10 minutes to 90 minutes. Also, a bath ratio of the dyeing is not particularly limited, for example, it may be within the range of 1:5 to 1:100, etc. To the aramid fibers after dyeing, washing by the ordinary method is carried out. In addition, reduction washing may be carried out in the same manner as in the dyeing step using a conventional disperse dye.

[0080] In this third embodiment, the following mentioned dyeing operation is subsequently carried out to the aramid fibers carried out the above-mentioned pre-dyeing step.

A. Dye Providing Step

[0081] The dye providing step in this third embodiment is carried out the same operations as those of the dye providing step in the above-mentioned first embodiment or the above-mentioned second embodiment.

B. Solvent Treatment Step

[0082] The solvent treatment step in this third embodiment is carried out by the same operations as those of the solvent treatment step in the above-mentioned first embodiment or the above-mentioned second embodiment.

C. Heat Treatment Step

[0083] In this third embodiment, the heat treatment step may be carried out, if necessary. Incidentally, when the heat treatment step is carried out in the third embodiment, the same operations as those of the heat treatment step in the above-mentioned second embodiment are carried out.

[0084] In this third embodiment, as mentioned above, by carrying out a series of the dyeing operation 1 or the dyeing operation 3 after carrying out the pre-dyeing step, a dyed product of the aramid fibers having a practical color depth, and good colorfastness, in particular, good colorfastness to light can be obtained.

[0085] Further, in this third embodiment, by carrying out the above-mentioned pre-dyeing step, the following effects can be obtained. First, by carrying out the pre-dyeing step using, for example, a disperse dye, a cationic dye or an acid dye, to the aramid fibers themselves, fuzz at the surfaces of the aramid fibers themselves are more sufficiently dyed, so that dyeing quality and color depth are further improved. On the other hand, when the aramid fibers are mixed with the other chemical fibers or natural fibers to form a mixed fiber, by carrying out the pre-dyeing step using a dye capable of dyeing these other fibers, hue of the aramid fibers and that of the other fibers can be unified, whereby the dyeing quality and the color depth of the dyed product are further improved.

(4) Fourth Embodiment

[0086] The dyeing method according to this fourth embodiment has a post-dyeing step which dyes the aramid fibers with a dye other than the vat dye and the sulfur dye after the dyeing operation 1 or the dyeing operation 3 explained in the above-mentioned first embodiment or the above-mentioned second embodiment. Incidentally, the above-mentioned dyeing operation 1 or the dyeing operation 3 carried out before the post-dyeing step may be carried out once alone, or may be repeated a plural number of times, depending on necessity. By repeating the dyeing operation 1 or the dyeing operation 3 a plural number of times, aramid fibers with a denser color can be obtained.
A. Dye Providing Step

[0087] The dye providing step in this fourth embodiment is carried out the same operations as those of the dye providing step in the above-mentioned first embodiment or the above-mentioned second embodiment.

B. Solvent Treatment Step

[0088] The solvent treatment step in this fourth embodiment is carried out by the same operations as those of the solvent treatment step in the above-mentioned first embodiment or the above-mentioned second embodiment.

C. Heat Treatment Step

[0089] In this fourth embodiment, the heat treatment step may be carried out, if necessary. Incidentally, when the heat treatment step is carried out in the fourth embodiment, the same operations as those of the heat treatment step in the above-mentioned second embodiment are carried out.

D2. Post-Dyeing Step

[0090] The post-dyeing step in this fourth embodiment is carried out by the same operations as those of the pre-dyeing step explained in the above-mentioned third embodiment. However, the aramid fibers to be dyed in the post-dyeing step have been already dyed by the vat dye or the sulfur dye in the above-mentioned dyeing operation 1 or the above-mentioned dyeing operation 3, which is different from the pre-dyeing step of the above-mentioned third embodiment.

[0091] In this fourth embodiment, as mentioned above, by carrying out the post-dyeing step after carrying out a series of the dyeing operation 1 or the dyeing operation 3, a dyed product of the aramid fibers having a practical color depth, and good colorfastness, in particular, good colorfastness to light can be obtained.

[0092] Further, in this fourth embodiment, by carrying out the above-mentioned post-dyeing step, the following effects can be obtained. First, by carrying out the post-dyeing step using, for example, a disperse dye, a cationic dye or an acid dye, to the aramid fibers themselves, fuzz at the surfaces of the aramid fibers themselves are more sufficiently dyed, so that dyeing quality and color depth are further improved. On the other hand, when the aramid fibers are mixed with the other chemical fibers or natural fibers to form a mixed fiber, by carrying out the post-dyeing step using a dye capable of dyeing these other fibers, hue of the aramid fibers and that of the other fibers can be unified, whereby the dyeing quality and the color depth of the dyed product are further improved.

EXAMPLES

[0093] In the following, based on the above-mentioned first embodiment to fourth embodiment, to the respective para-type aramid fibers, para-type copolymerized aramid fiber and meta-type aramid fibers, dyeing of the following respective Examples and Comparative Examples was carried out.

Example 1

[0094] In this Example 1, N-methyl-2-pyrrolidone was used as a polar solvent, fabrics (hereinafter referred to as “aramid fabrics”) comprising the aramid fibers were dyed based on the above-mentioned second embodiment. In this Example 1, twilled fabrics (hereinafter referred to as “para-type aramid fabrics”) having an areal weight of 244 g/m² and using No. 20 count two folded yarns comprising 100% by weight of para-type aramid fibers as warp yarns and weft yarns, twilled fabrics (hereinafter referred to as “para-type copolymerized aramid fabrics”) having an areal weight of 244 g/m² and using No. 20 count two folded yarns comprising 100% by weight of para-type copolymerized aramid fibers as warp yarns and weft yarns, and twilled fabrics (hereinafter referred to as “meta-type aramid fabrics”) having an areal weight of 200 g/m² and using No. 40 count two folded yarns comprising 100% by weight of meta-type aramid fibers as warp yarns and weft yarns were used. These aramid fabrics were used after desizing and degumming by the ordinary method.

A. Dye Providing Step

[0095] Dye providing procedure was carried out by a continuous method using a mangle device for testing, and each of the aramid fabrics was subjected to pad and nip a dyeing solution containing a vat dye to provide the vat dye thereto. The pickup rates at this time were each 61% by weight for the para-type aramid fabrics, 58% by weight for the para-type copolymerized aramid fabrics, and 67% by weight for the meta-type aramid fabrics.

[0096] As the dyeing solution, 50 g/L of a vat dye was dispersed in an unreduced state, and TAMANORI SA-25 (Arakawa Chemical Industries, Ltd.; hereinafter referred to as “TAMANORI”) was used as a migration preventive agent in combination. The used dye was Mikenethren Blue BC superfine (C.I. Vat Blue 6, vat dye available from DyStar Japan Ltd.).

[0097] Drying was carried out by using a baking box device for testing, and each of the aramid fabrics after providing the dyeing solution was dried at 105°C for 5 minutes, to adhere the vat dye onto the surfaces of the fibers of each of the aramid fabrics. Each of the aramid fabrics after drying was injected into a subsequent solvent treatment step (N-methyl-2-pyrrolidone treatment step) as such without carrying out washing or reduction washing.

B. Solvent Treatment Step (N-methyl-2-pyrrolidone Treatment Step)

[0098] N-methyl-2-pyrrolidone was used as a polar solvent, and treatment was carried out by an aqueous solution with a concentration of 60% by weight. For providing the treating solution, a mangle device for testing was used, and each of the aramid fabrics after the dye providing step was subjected to the solvent treatment by a continuous method. The treatment temperature at this time was 20°C. The treatment was carried out by immersing the aramid fabrics in the treating solution for 1 second and immediately squeezed by the mangle. A pickup rate at this time was each 59% by weight for the para-type aramid fabrics, 59% by weight for the para-type copolymerized aramid fabrics, and 62% by weight for the meta-type aramid fabrics.

C. Heat Treatment Step

[0099] For the heat treatment, a baking box device for testing was used, and each of the aramid fabrics after the solvent treatment was carried out a dry heat treatment at 105°C for 5 minutes to adhere the vat dye onto each of the aramid fabrics. Each of the aramid fabrics after the heat treatment was dried after removing the remaining N-methyl-2-pyrrolidone by washing with water and washing with hot water.
Next, reduction washing of each of the dyed aramid fabrics after the heat treatment step was carried out. The reduction washing was carried out to remove the undying vat dye remaining at the surface of the fibers and to improve colorfastness. The conditions of the reduction washing were the same as those of the dyeing of the polyester fibers by a disperse dye, and the treatment was carried out by using 1 g/L of sodium dithionite as a reducing agent in combination with 1 g/L of sodium hydroxide at 80°C for 1 minute, thereafter, washing with hot water and washing with water were carried out and then the fabrics were dried to obtain each of the aramid fabrics of Example 1 dyed to navy blue and having a practical color depth.

Comparative Example 1

Similarly to the above-mentioned Example 1, a material in which the dye providing step alone of each of the aramid fabrics has been carried out, and the solvent treatment step and the heat treatment step have not been carried out was made Comparative Example 1. More specifically, the dye providing procedure was carried out under the same conditions as those of the above-mentioned Example 1, and reduction washing of each of the aramid fabrics after providing the vat dye was carried out. The reduction washing was carried out under the same conditions as those of the above-mentioned Example 1, thereafter, washing with hot water and washing with water were carried out and then the fabrics were dried to obtain each of the aramid fabrics of Comparative Example 1.

Each of the dyed aramid fabrics of Example 1 and Comparative Example 1 which have been dyed as mentioned above was evaluated as mentioned below.

Color Depth (Total K/S Value):

A surface color depth of each of the dyed aramid fabrics was shown as a total K/S value. When the total K/S value is larger, it means that the aramid fabrics are dyed by a dense color. The total K/S means a total value of 16 K/S values at 16 wavelengths measured at 20 nm intervals in the measured range of wavelengths of from 400 nm to 700 nm. The K/S value can be obtained from a reflectance R at the respective wavelengths from the following mentioned Kubelka-Munk equation. Here, K represents an extinction coefficient, and S represents a light scattering coefficient.

\[ K/S = \frac{(1-R)^2}{2R} \]

Incidentally, the value of the reflectance R at the respective wavelengths was measured by using a spectrophotometer UV-3100 (manufactured by Shimadzu Corporation) on which an integrating sphere has been mounted. With regard to each of the aramid fabrics, the total K/S values obtained by calculating according to the above formula were shown in Table 1.

Lightness (L* Value)

A degree of the dense color of each of the dyed aramid fabrics was evaluated by lightness (L* value) in the above-mentioned L*a*b* colorimetric system. The L* value is shown in the range of 100 (white) to 0 (black), and the L* value is smaller, then, it is evaluated to as a denser color. Incidentally, the L* value was measured by using a color difference meter CR-200 (manufactured by Minolta Camera Co., Ltd.). The obtained L* values of each of the aramid fabrics are shown in Table 1.

Colorfastness:

Other than the above-mentioned color depth (total K/S value) and lightness (L* value), colorfastness was confirmed as a basic evaluation item of the dyed product. In particular, colorfastness to light (JIS 10842) which is assumed to be a problem in colorfastness of the aramid fibers was evaluated. Colorfastness to light of the aramid fibers is difficulty evaluated since fibers themselves change yellowish brown in addition to discoloration of the dye due to photoirradiation, so that it was evaluated as mentioned below. Irradiation with fourth grade of blue scale was carried out to each of the aramid fabrics, and the change was judged by the grade of gray scale for discoloration. Incidentally, judgment of the grade was, in addition to the five grades from the first grade (failure) to the fifth grade (good), intermediate evaluation of the respective grades was also carried out. For example, an evaluation between the third grade and the fourth grade was mentioned as 3-4 grades. The evaluation results are shown in Table 1.

| TABLE 1 |
|-----------------|-----------------|-----------------|-----------------|
| <<Each Aramid fabrics>> | <<Vat dye>> | <<N-methyl-2-pyridylidone>> |
| Aramid fabrics | Color depth (Total K/S value) | Lightness (L* value) | Colorfastness to light (grade) |
| Aramid fabrics | Color depth (Total K/S value) | Lightness (L* value) | Colorfastness to light (grade) |
| para-type | 72.3 | 36.4 | 4 |
| para-type coolymerized | 85.0 | 31.1 | 4-5 |
| meta-type | 50.3 | 35.2 | 3-4 |

As can be seen from Table 1, in Example 1, either of the respective aramid fabrics had the practical color depth (total K/S value) and lightness (L* value), and each also had good colorfastness to light. Further, whereas it is not shown in Table 1, in each of the dyed aramid fabrics of Example 1, the fabrics had maintained the practical properties of high performance fibers without generating color unevenness or dimensional change, or lowering in physical properties markedly. On the other hand, in Comparative Example 1, as compared with those of Example 1, in either of the respective aramid fabrics, color depth, lightness and colorfastness to light were inferior, in particular, color depth, lightness and colorfastness to light of the meta-type aramid fabrics were insufficient.

Example 2

In this Example 2, aramid fabrics were dyed based on the above-mentioned second embodiment and N-methyl-2-pyridylidone was used as a polar solvent. In this Example 2, twilled fabrics (hereinunder referred to as "mixed spinning aramid fabrics") having an areal weight of 160 g/m² and using No. 40 count two folded yarns in which 95% by weight of meta-type aramid fibers and 5% by weight of para-type copo-
polymerized aramid fibers had been mixed spinning as warp yarns and weft yarns were used. This mixed spinning aramid fabrics were used after desizing and degumming by the ordinary method.

A. Dye Providing Step

[0109] The same operations as in the above-mentioned Example 1 were carried out except for changing the dye to be used to the sulfur dye mentioned below in the above-mentioned Example 1. A pickup rate at this time was 80% by weight. As the dyeing solution, 50 g/L of the sulfur dye was dispersed in an unreduced state, and TAMANORI was used in combination as a migration preventive agent. The sulfur dye used was Asahiio Blue RC200 (C.I. Sulphur Blue 7, sulfur dye available from Asahi Kagaku Kogyo Co., Ltd.).

[0110] Drying was carried out in the same manner as in the above-mentioned Example 1, and the mixed spinning aramid fabrics after providing the dyeing solution thereto was dried at 105°C for 5 minutes to adhere the sulfur dye on the surfaces of the fibers of the mixed spinning aramid fabrics. The mixed spinning aramid fabrics after drying was injected into the subsequent solvent treatment step (N-methyl-2-pyrrolidone treatment step) as such without carrying out washing or reduction washing.

B. Solvent Treatment Step (N-methyl-2-pyrrolidone Treatment Step)

[0111] In this Example 2, N-methyl-2-pyrrolidone which is the same as in the above-mentioned Example 1 was used as a polar solvent, but the treatment was carried out with a concentration of 100% by weight. For providing the treating solution, a mangle device for testing was used, and the mixed spinning aramid fabrics after the dye providing step were subjected to the solvent treatment by a continuous method. The treatment temperature at this time was 50°C.

[0112] The treatment was carried out by immersing the mixed spinning aramid fabrics into the treating solution for 1 second and then immediately squeezed by the mangle. A pickup rate at this time was 88% by weight.

C. Heat Treatment Step

[0113] The heat treatment was carried out in the same manner as in the above-mentioned Example 1, and by using a baking box device for testing, dry heat treatment of the mixed spinning aramid fabrics after the solvent treatment was carried out at 105°C for 5 minutes to adhere the sulfur dye onto the mixed spinning aramid fabrics. The mixed spinning aramid fabrics after the heat treatment were dried after removing the remaining N-methyl-2-pyrrolidone by washing with hot water and washing with water, to obtain mixed spinning aramid fabrics of Example 2 dyed to navy blue and having a practical color depth.

Comparative Example 2

[0114] Similarly to the above-mentioned Example 2, a material in which the dye providing step alone of each of the aramid fabrics has been carried out, and the solvent treatment step and the heat treatment step have been carried out was made Comparative Example 2. More specifically, the mixed spinning aramid fabrics which have been carried out the dye providing step under the same conditions as those of the above-mentioned Example 2 to provide the sulfur dye were subjected to washing with hot water and washing with water, and drying to obtain mixed spinning aramid fabrics of Comparative Example 2 which were dyed to navy blue.

[0115] The dyed mixed spinning aramid fabrics of Example 2 and Comparative Example 2 which had been dyed as mentioned above were evaluated in the same manner as in the above-mentioned Example 1. The evaluation results of the total K/S value which evaluates the color depth, lightness (L* value) which evaluates the degree of a dark color and colorfastness to light are shown in Table 2.

<table>
<thead>
<tr>
<th></th>
<th>Example 2</th>
<th>Comparative Example 2</th>
</tr>
</thead>
<tbody>
<tr>
<td>Color depth</td>
<td>108.2</td>
<td>39.8</td>
</tr>
<tr>
<td>Lightness (L*)</td>
<td>27.1</td>
<td>44.0</td>
</tr>
<tr>
<td>Colorfastness to light (grade)</td>
<td>3-4</td>
<td>3</td>
</tr>
</tbody>
</table>

[0116] As can be seen from Table 2, in Example 2, mixed spinning aramid fabrics having a practical color depth (total K/S value) and lightness (L* value) could be obtained. Also, the mixed spinning aramid fabrics of Example 2 have good colorfastness to light. Further, whereas it is not shown in Table 2, in the dyed mixed spinning aramid fabrics of Example 2, the fabrics had maintained the practical properties of high performance fibers without generating color unevenness or dimensional change, or lowering in physical properties markedly. On the other hand, in Comparative Example 2, as compared with those of Example 2, both of color depth and lightness were markedly inferior, and colorfastness to light was also low so that no practically dyed product was obtained.

Example 3

[0117] In this Example 3, aramid fabrics were dyed based on the above-mentioned second embodiment and N-methyl-2-pyrrolidone was used as a polar solvent. In this Example 3, to each of the dyed aramid fabrics obtained in the above-mentioned Example 1 were repeated the same dyeing operations as the above-mentioned Example 1 a plural number of times. More specifically, the above-mentioned Example 1 was made the dyeing operation once, and the dyeing operation in which the dye providing step, the solvent treatment step and the heat treatment step had been combined was further repeated to carry out a total of 3 times, a total of 5 times and a total of 7 times of the dyeing operations. However, the reduction washing was carried out at after the final dyeing operation alone.

[0118] Each of the dyed aramid fabrics of Example 3 which had been dyed as mentioned above were evaluated in the same manner as in the above-mentioned Example 1. The evaluation results of the total K/S value which evaluates the color depth, lightness (L* value) which evaluates the degree of a dark color and colorfastness to light are shown in Table 3.
As can be seen from Table 3, in each of the aramid fabrics, as compared with Example 1 in which the dyeing operation is once, as a number of the dyeing operation increases, the color depth (total K/S value) is markedly improved, and lightness (L* value) becomes small as substantially around 30 or lower, and each of the aramid fabrics with a very dark color can be obtained. Each of these aramid fabrics with a very dark color have had good colorfastness to light as shown in Table 3. Further, whereas it is not shown in Table 3, in each of the dyed aramid fabrics of Example 3, the fabrics had maintained the practical properties of high performance fibers without generating color unevenness or dimensional change, or lowering in physical properties markedly.

Example 4

In this Example 4, aramid fabrics were dyed based on the above-mentioned second embodiment and N-methyl-2-pyrroolidone was used as a polar solvent. In this Example 4, to each of the aramid fabrics which are similar to the above-mentioned Example 1 were repeated the dyeing operations by the vat dye with a plural number of times in the same manner as in the above-mentioned Example 3. However, the used vat dye was Indanthren Brilliant Pink R (C.I. Vat Red 1, vat dye available from DyStar Japan Ltd.). More specifically, the above-mentioned Example 1 was made the dyeing operation once, and the dyeing operation in which the dye providing solvent step, the solvent treatment step and the heat treatment step had been combined was further repeated to carry out a total of 2 times and a total of 3 times of the dyeing operations. However, the reduction washing was carried out at after the final dyeing operation alone.

Each of the dyed aramid fabrics of Example 4 which had been dyed as mentioned above were evaluated in the same manner as in the above-mentioned Example 1. The evaluation results of the total K/S value which evaluates the color depth, lightness (L* value) which evaluates the degree of a dark color and colorfastness to light are shown in Table 4.

As can be seen from Table 4, in each of the aramid fabrics, as compared with the case where the dyeing operation is once, as a number of the dyeing operation increases, the color depth (total K/S value) is markedly improved, and each of the aramid fabrics with a dark color can be obtained. Whereas the lightness (L* value) is larger than 38, this is because the dye used is “Pink R”. This Example 4 is a prescription to dye a vivid red, which is not a prescription to obtain a dark color such as navy blue and black. On the other hand, each of the aramid fabrics has good colorfastness to light as shown in Table 4. Further, whereas it is not shown in Table 4, in each of the dyed aramid fabrics of Example 4, the fabrics had maintained the practical properties of high performance fibers without generating color unevenness or dimensional change, or lowering in physical properties markedly.

Example 5

In this Example 5, aramid fabrics were dyed according to the above-mentioned fourth embodiment (dyeing by a vat dye →post-dyeing by a disperse dye) and N-methyl-2-pyrroolidone was used as a polar solvent. In this Example 5, to each of the dyed aramid fabrics by the vat dye obtained in the above-mentioned Example 1, a post-dyeing step using a disperse dye was carried out subsequently.

D2. Post-Dyeing Step by Disperse Dye

Dyeing was carried out by the immersion dyeing method using a disperse dye, and each of the aramid fabrics after dyed by the vat dye obtained in the above-mentioned Example 1 was dyed by using a high temperature and high pressure dyeing tester MINI-COLOR (manufactured by TEXAM Giken Co., Ltd.) without reduction washing. As the dyeing solution, 5% owf of Dianix Blue FBL-E (C.I. Disperse Blue 56, disperse dye available from DyStar Japan Ltd.) was used, and an acetic acid/sodium acetate series buffer with a pH 5 was used in combination.

As a dyeing method, a high temperature and high pressure dyeing was carried out by making a bath ratio of 1:100, and under the conditions at 135° C. for 60 minutes. Reduction washing was carried out to each of the aramid fabrics after the dyeing in the same manner as in the dyeing of ordinary polyester fibers by a disperse dye. The reduction washing was carried out under the conditions of using 1 g/L of sodium dithionite as a reducing agent in combination with 1 g/L of sodium hydroxide at 80° C. for 1 minute, thereafter,
washing with hot water and washing with water were carried out and then the fabrics were dried to obtain each of the aramid fabrics of Example 5 dyed to navy blue which is a very dark color.

Comparative Example 3

Similarly to the above-mentioned Example 5, a material in which each of the aramid fabrics had been carried out dyeing by the disperse dye alone was made Comparative Example 3. More specifically, none of the dyeing operations comprising the dye providing step, the solvent treatment step or the heat treatment step according to the present invention was carried out, but the dyeing step with a disperse dye alone which is the same as that of the above-mentioned Example 5 was carried out, thereafter, reduction washing, washing with hot water and washing with water were carried out in the same manner as in Example 5, and the fabrics were dried to obtain each of the aramid fabrics of Comparative Example 3 dyed to navy blue.

Comparative Example 4

Also, similarly to the above-mentioned Example 5, a material in which each of the aramid fabrics had been carried out the solvent treatment step, the heat treatment step and the dyeing step by a disperse dye alone was made Comparative Example 4. More specifically, the solvent treatment step and the heat treatment step alone were carried without carrying out the dye providing step which is to provide a vat dye, and then, the dyeing step with a disperse dye which is the same as in the above-mentioned Example 5 was carried out, thereafter, reduction washing, washing with hot water and washing with water were carried out in the same manner as in Example 5, and the fabrics were dried to obtain each of the aramid fabrics of Comparative Example 4 dyed to navy blue.

Each of the dyed aramid fabrics of Example 5, Comparative Example 3 and Comparative Example 4 which had been dyed as mentioned above were evaluated in the same manner as in the above-mentioned Example 1. The evaluation results of the total K/S value which evaluates the color depth, lightness (L* value) which evaluates the degree of a dark color and colorfastness to light are shown in Table 5.

<table>
<thead>
<tr>
<th>Aramid fabrics</th>
<th>Dye</th>
<th>Color depth (Total K/S value)</th>
<th>Lightness (L* value)</th>
<th>Colorfastness to light (grade)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Example 5</td>
<td>Vat + Disperse</td>
<td>110.2</td>
<td>29.0</td>
<td>4-5</td>
</tr>
<tr>
<td>Example 1</td>
<td>Vat Disperse</td>
<td>72.3</td>
<td>36.4</td>
<td>4</td>
</tr>
<tr>
<td>Comparative example 3</td>
<td>Disperse</td>
<td>67.8</td>
<td>40.8</td>
<td>3-4</td>
</tr>
<tr>
<td>Comparative example 4</td>
<td>Disperse</td>
<td>71.7</td>
<td>39.4</td>
<td>3-4</td>
</tr>
<tr>
<td>Example 5</td>
<td>Vat + Disperse</td>
<td>124.6</td>
<td>27.7</td>
<td>5</td>
</tr>
<tr>
<td>Example 1</td>
<td>Vat Disperse</td>
<td>85.0</td>
<td>31.1</td>
<td>4-5</td>
</tr>
<tr>
<td>Comparative example 3</td>
<td>Disperse</td>
<td>31.3</td>
<td>55.1</td>
<td>3-4</td>
</tr>
</tbody>
</table>

As can be seen from Table 5, as compared with Example 1 dyed by the vat dye alone, in Example 5 in which the fibers are further dyed by a disperse dye, each of the aramid fabrics markedly improved in color depth (total K/S value), having small lightness (L* value) of 30 or less, with a very dark color can be obtained. Each of the aramid fabrics with the very dark color has better colorfastness to light than that of Example 1 as shown in Table 5. Also, in each of the aramid fabrics of this Example 5, fuzz at the surfaces of the fabrics have been dyed by both of the vat dye and the disperse dye to a very dark color, and surface quality of the fabrics has been more improved. Further, whereas it is not shown in Table 5, in each of the dyed aramid fabrics of Example 5, the fabrics had maintained the practical properties of high performance fibers without generating color unevenness or dimensional change, or lowering in physical properties markedly.

On the other hand, in Comparative Example 3, as compared with those of Example 5, color depth and lightness were inferior thereto in either of the respective aramid fabrics. In addition, these respective aramid fabrics were dyed only by the disperse dye, and colorfastness to light was insufficient as compared with those of Example 5 and Example 1. Also, in Comparative Example 4, by the effects of the solvent treatment, the color depth and lightness by the disperse dye are improved than those of Comparative Example 3. However, the respective aramid fabrics of Comparative Example 4 are inferior to those of Example 5 in both of the color depth and lightness. Moreover, these respective aramid fabrics of Comparative Example 4 were dyed only by the disperse dye, and colorfastness to light was insufficient as compared with those of Example 5.

Example 6

In this Example 6, aramid fabrics were dyed based on the above-mentioned first embodiment and using sulfenic acid as a polar solvent. In this Example 6, the same mixed spinning aramid fabrics as those of the above-mentioned Example 2 were used. This mixed spinning aramid fabrics were used after desizing and degumming by the ordinary method.

A. Dye Providing Step
Example 1, or the vat dye "Indanthren Brilliant Pink R" which is the same as used in the above-mentioned Example 4 was used. The operations in the dyeing providing step were carried out in the same manner as in the above-mentioned Example 1. A pickup rate at this time was 80% by weight.

Drying was carried out in the same manner as in the above-mentioned Example 1, and the mixed spinning aramid fabrics after providing the dyeing solution was dried at 105°C for 5 minutes to adhere the vat dye onto the surfaces of the fibers of the mixed spinning aramid fabrics. The mixed spinning aramid fabrics after drying was injected into the subsequent solvent treatment step (sulfuric acid treatment step) as such without carrying out washing or reduction washing.

B. Solvent Treatment Step (Sulfuric Acid Treatment Step)

The sulfuric acid treatment was carried out by the continuous method, using a mangle device for testing, and the sulfuric acid treatment was carried out to the mixed spinning aramid fabrics after the dye providing step. A concentration of the used aqueous sulfuric acid solution was 77% by weight, and a treatment temperature was 20°C. After immersion, the fabrics were squeezed by the mangle to make a pickup rate 156% by weight, and then, immediately washed with water and neutralized by an aqueous sodium carbonate solution, and washed with water. An immersion time in the aqueous sulfuric acid solution was 30 seconds. The mixed spinning aramid fabrics after the solvent treatment step was sufficiently washed with water and then dried.

Next, reduction washing was carried out to the dyed mixed spinning aramid fabrics after the sulfuric acid treatment. The reduction washing was carried out under the same conditions as those of the above-mentioned Example 1, thereafter, washing with hot water and washing with water were carried out and dried to obtain mixed spinning aramid fabrics of Example 6 having a practical color depth.

<table>
<thead>
<tr>
<th>Table 6</th>
<th>Mixed spinning Aramid fabrics x Vat dyes x Sulfuric acid</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>Example 6</td>
</tr>
<tr>
<td>Vat dye</td>
<td>Color depth (Total K/S value)</td>
</tr>
<tr>
<td></td>
<td>Lightness (L* value)</td>
</tr>
<tr>
<td></td>
<td>Colorfastness to light (grade)</td>
</tr>
<tr>
<td>Blue BC</td>
<td>86.6</td>
</tr>
<tr>
<td></td>
<td>31.0</td>
</tr>
<tr>
<td></td>
<td>4</td>
</tr>
<tr>
<td>Pink R</td>
<td>62.3</td>
</tr>
<tr>
<td></td>
<td>45.7</td>
</tr>
<tr>
<td></td>
<td>4-5</td>
</tr>
</tbody>
</table>

As can be seen from Table 6, in Example 6, the mixed spinning aramid fabrics having a practical color depth (total K/S value) and lightness (L* value) can be obtained by using the vat dye "Blue BC". On the other hand, in the vat dye "Pink R" of Example 6, it is a prescription for dyeing a vivid red in the same manner as in the above-mentioned Example 4, so that lightness (L* value) does not show a small value. However, in the vat dye "Pink R", the mixed spinning aramid fabrics having a practical color depth (total K/S value) can be obtained. Also, the mixed spinning aramid fabrics of Example 6 each have good colorfastness to light. Further, whereas it is not shown in Table 6, in the dyed mixed spinning aramid fabrics of Example 6, the fabrics had maintained the practical properties of high performance fibers without generating color unevenness or dimensional change, or lowering in physical properties markedly. On the other hand, in Comparative Example 5, as compared with Example 6, both of the color depth and colorfastness to light were inferior, and no practically dyed product can be obtained.

Example 7

Similarly to the above-mentioned Example 6, the dyeing providing step alone was carried out to the mixed spinning aramid fabrics without carrying out the sulfuric acid treatment, which was made Comparative Example 5. More specifically, reduction washing was carried out to the mixed spinning aramid fabrics which had been carried out the dye providing step under the same conditions as those of the above-mentioned Example 1 to provide the vat dye. The reduction washing was carried out under the same conditions as those of the above-mentioned Example 1, thereafter, washing with hot water and washing with water were carried out and then the fabrics were dried to obtain mixed spinning aramid fabrics of Comparative Example 5.

The dyed mixed spinning aramid fabrics of Example 6 and Comparative Example 5 which had been dyed as mentioned above were evaluated in the same manner as in the above-mentioned Example 1. The evaluation results of the total K/S value which evaluates the color depth, lightness (L* value) which evaluates the degree of a dark color and colorfastness to light are shown in Table 6.
As can be seen from Table 7, as compared with Example 6 in which the dyeing operation is once, in Example 7, as a number of the dyeing operation increases, the color depth (total K/S value) is markedly improved, and lightness (I* value) becomes small as 25 or less, and the mixed spinning aramid fabrics with a very dark color can be obtained. These mixed spinning aramid fabrics with a very dark color have had good colorfastness to light as shown in Table 7. Further, whereas it is not shown in Table 7, in the dyed mixed spinning aramid fabrics of Example 7, the fabrics had maintained the practical properties of high performance fibers without generating color unevenness or dimensional change, or lowering in physical properties markedly.

Example 8

In this Example 8, aramid fabrics were dyed based on the above-mentioned first embodiment and sulfuric acid was used as a polar solvent. In this Example 8, the dyeing operation by the sulfur dye was carried out to the same mixed spinning aramid fabrics as in Example 6. The mixed spinning aramid fabrics were used after desizing and degumming by the ordinary method in the same manner as in the above-mentioned Example 6.

A. Dye Providing Step

In this Example 8, similarly to the above-mentioned Example 6, the same operations as in the above-mentioned Example 6 were carried out except for changing the dye to be used to the following mentioned sulfur dye. A pickup rate at this time was 80% by weight. As the dyeing solution, 50 g/L of the sulfur dye was dispersed in an unreduced state, and TAMANORI was used as a migration preventive agent in combination. The sulfur dyes used were Asathiosol Yellow S-RR (C.I. No. unknown, sulfur dye available from Asahi Kagaku Kogyo Co., Ltd.), Asathiosol Bordeaux S-3B (C.I. Sulphur Red 6, sulfur dye available from Asahi Kagaku Kogyo Co., Ltd.), Asathiosol Blue RC200 (C.I. Sulphur Blue 7, sulfur dye available from Asahi Kagaku Kogyo Co., Ltd.), and Asathiosol Indigo Green S-BG (C.I. Sulphur Blue 15, sulfur dye available from Asahi Kagaku Kogyo Co., Ltd.).

Drying was carried out in the same manner as in the above-mentioned Example 6, and the mixed spinning aramid fabrics after providing the dyeing solution thereto was dried at 105°C for 5 minutes to adhere the sulfur dye onto the surfaces of the fibers of the mixed spinning aramid fabrics. The mixed spinning aramid fabrics after drying was injected into the subsequent solvent treatment step (sulfuric acid treatment step) as such without carrying out washing or reduction washing.

B. Solvent Treatment Step (Sulfuric Acid Treatment Step)

In this Example 8, the sulfuric acid treatment was carried out to the mixed spinning aramid fabrics after the dye providing step in the same manner as in the above-mentioned Example 6. A concentration of the used aqueous sulfuric acid solution was 77% by weight, a treatment temperature was 20°C and an immersing time was 30 seconds. A pickup rate at this time was 156% by weight, and washing with water, neutralization and washing with water were carried out in the same manner as in the above-mentioned Example 6, and the fabrics were dried to obtain mixed spinning aramid fabrics of Example 8 having a practical color depth.

Comparative Example 6

Similarly to the above-mentioned Example 8, the dye providing step alone was carried out to the mixed spinning aramid fabrics without carrying out the sulfuric acid treatment which was made Comparative Example 6. More specifically, the mixed spinning aramid fabrics carrying out the dye providing step in the same conditions as those of the above-mentioned Example 8 to provide the sulfur dye was washed with water and dried to obtain mixed spinning aramid fabrics of Comparative Example 6.

The dyed mixed spinning aramid fabrics of Example 8 and Comparative Example 6 which had been dyed as mentioned above were evaluated in the same manner as in the above-mentioned Example 1. However, lightness (I* value) was not measured. The evaluation results of the total K/S value which evaluates the color depth and colorfastness to light are shown in Table 8.
Example 9

[0150] In this Example 9, aramid fabrics were dyed based on the above-mentioned first embodiment and sulfuric acid was used as a polar solvent. In this Example 9, as the aramid fibers mainly comprising the para-type aramid fibers, twilled fabrics (hereinafter referred to as “para-type single yarn aramid fabrics”) having an areal weight of 144 g/m² and using No. 20 count single yarn comprising 100% by weight of para-type aramid fibers as warp yarns and weft yarns were used. The para-type single yarn aramid fabrics were used after desizing and degumming by the ordinary method.

[0151] In this Example 9, the dyeing providing step and the solvent treatment step (sulfuric acid treatment step) were carried out in the same operation conditions and the same dyes used in the above-mentioned Example 6. A pickup rate at the dyeing providing step at this time was 61% by weight, and a pickup rate at the solvent treatment step was 126% by weight. After carrying out the dyeing operation by the vat dye according to the above, reduction washing was carried out in the same manner as in the above-mentioned Example 1 to obtain para-type single yarn aramid fabrics of Example 9 having a practical color depth.

Comparative Example 7

[0152] Similarly to the above-mentioned Example 9, the dye providing step alone was carried out to the para-type single yarn aramid fabrics without carrying out the sulfuric acid treatment, which was made Comparative Example 7. More specifically, reduction washing was carried out with the same conditions as in Example 1 to the para-type single yarn aramid fabrics which had been carried out the dye providing step with the same conditions as in the above-mentioned Example 9 to provide the vat dye. Thereafter, washing with hot water and washing with water were carried out and the fabrics were dried to obtain para-type single yarn aramid fabrics of Comparative Example 7.

[0153] The dyed para-type single yarn aramid fabrics of Example 9 and Comparative Example 7 which had been dyed as mentioned above were evaluated in the same manner as in the above-mentioned Example 1. However, lightness (L* value) was not measured. The evaluation results of the total K/S value which evaluates the color depth and colorfastness to light are shown in Table 9.

<table>
<thead>
<tr>
<th></th>
<th>Example 9</th>
<th>Comparative Example 7</th>
</tr>
</thead>
<tbody>
<tr>
<td><strong>Var dye</strong></td>
<td></td>
<td></td>
</tr>
<tr>
<td>Blue BC</td>
<td>50.0</td>
<td>30.0</td>
</tr>
<tr>
<td>Pink R</td>
<td>47.0</td>
<td>31.7</td>
</tr>
</tbody>
</table>

[0154] As can be seen from Table 9, in Example 9, the fabrics had maintained the practical properties of high performance fibers without generating color unevenness or dimensional change, or lowering in physical properties markedly. On the other hand, in Comparative Example 7, as compared with Example 9, both of the color depth and colorfastness to light are inferior, and no practically dyed product can be obtained.

Example 10

[0155] In this Example 10, aramid fabrics were dyed based on the above-mentioned first embodiment and sulfuric acid was used as a polar solvent. In this Example 10, among the dyed para-type single yarn aramid fabrics obtained in the above-mentioned Example 9, the same dyeing operation which is the same as in the above-mentioned Example 9 was repeated to the para-type yarn aramid fabrics dyed by the vat dye “Mikethen Blue BC superfine” with a plural number of times. More specifically, the above-mentioned Example 9 was made the dyeing operation once, and the dyeing operation in which the dye providing step and the solvent treatment step (sulfuric acid treatment step) had been combined was further repeated to carry out a total of 3 times, a total of 5 times and a total of 7 times of the dyeing operations. However, the reduction washing was carried out at after the final dyeing operation alone.

[0156] The dyed para-type single yarn aramid fabrics of Example 10 which had been dyed as mentioned above were evaluated in the same manner as in the above-mentioned Example 1. However, lightness (L* value) was not measured. The evaluation results of the total K/S value which evaluates the color depth and colorfastness to light are shown in Table 10.

<table>
<thead>
<tr>
<th></th>
<th>Example 9</th>
<th>Example 10</th>
</tr>
</thead>
<tbody>
<tr>
<td><strong>Color depth</strong></td>
<td>50.0</td>
<td>50.0</td>
</tr>
<tr>
<td><strong>Colorfastness to light</strong></td>
<td>3-4</td>
<td>5-7</td>
</tr>
</tbody>
</table>

[0157] As can be seen from Table 10, as compared with Example 9 in which the dyeing operation is once, in Example 10, as a number of the dyeing operation increases, the color depth (total K/S value) is markedly improved, and the aramid fabrics with a very dark color can be obtained. These para-type single yarn aramid fabrics with a very dark color have had good colorfastness to light as shown in Table 10. Further, whereas it is not shown in Table 10, in the dyed para-type single yarn aramid fabrics of Example 10, the fabrics had maintained the practical properties of high performance fibers without generating color unevenness or dimensional change, or lowering in physical properties markedly.

Example 11

[0158] In this Example 11, aramid fabrics were dyed based on the above-mentioned fourth embodiment and sulfuric acid was used as a polar solvent. In this Example 11, the same
mixed spinning aramid fabrics as those used in the above-mentioned Example 6 was used. The mixed spinning aramid fabrics were used after desizing and degumming by the ordinary method.

A. Dye Providing Step

**[0159]** In this Example 11, the same operations were carried out as in the above-mentioned Example 1 except for using 60 g/L of Mikethren Grey M super-fine (C.I. Vat Black 8, vat dye available from DyStar Japan Ltd.) as the vat dye. A pickup rate at this time was 80% by weight.

**[0160]** Drying was carried out in the same manner as in the above-mentioned Example 1, and the mixed spinning aramid fabrics after providing the dyeing solution was dried at 105°C for 5 minutes to adhere the vat dye onto the surfaces of the fibers of the mixed spinning aramid fabrics. The mixed spinning aramid fabrics after drying was injected into the subsequent solvent treatment step (sulfuric acid treatment step) as such without carrying out washing or reduction washing.

B. Solvent Treatment Step (Sulfuric Acid Treatment Step)

**[0161]** The sulfuric acid treatment was carried out by the continuous method, using a mangle device for testing, and the sulfuric acid treatment was carried out to the mixed spinning aramid fabrics after the dye providing step. A concentration of the used aqueous sulfuric acid solution was 80% by weight, and a treatment temperature was 20°C. After immersion, the fabrics were squeezed by the mangle to make a pickup rate 80% by weight, and then, immediately washed with water and neutralized by an aqueous sodium carbonate solution, and washed with water. An immersion time in the aqueous sulfuric acid solution was 20 seconds. In this Example 11, the mixed spinning aramid fabrics after the solvent treatment step (sulfuric acid treatment step) were injected into the subsequent post-dyeing step by a disperse dye without drying.

D2. Post-Dyeing Step by Disperse Dye

**[0162]** Dyeing was carried out by the immersion dyeing method using a disperse dye, and the mixed spinning aramid fabrics after the sulfuric acid treatment was dyed by using a high temperature and high pressure dyeing tester MINICOLOR (manufactured by TEXAM Giken Co., Ltd.) without drying as mentioned above. As the dyeing solution, 10% owf of Kayalon Polyester Navy Blue NII-E (C.I. No. unknown, disperse dye available from NIPPON KAYAKU Co., Ltd.) was used and an acetic acid/sodium acetate series buffer having a pH of 5 was used in combination.

**[0163]** As a dyeing method, a high temperature and high pressure dyeing was carried out by making a bath ratio of 1:100, and under the conditions at 130°C for 60 minutes. Reduction washing was carried out to the mixed spinning aramid fabrics after the dyeing in the same manner as in the dyeing of ordinary polyester fibers by a disperse dye. The reduction washing was carried out under the same conditions of the post-dyeing step of the above-mentioned Example 5, thereafter, washing with hot water and washing with water were carried out and then the fabrics were dried to obtain mixed spinning aramid fabrics of Example 11 dyed to black which is a very dark color.

Comparative Example 8

**[0164]** Similarly to the above-mentioned Example 11, a material in which the dyeing step by the disperse dye alone was carried out to the undying mixed spinning aramid fabrics was made Comparative Example 8. In this Comparative Example 8, the conditions of the dyeing step by the disperse dye were made the same as those of the above-mentioned Example 11.

Comparative Example 9

**[0165]** Similarly to the above-mentioned Example 11, the solvent treatment step (sulfuric acid treatment step) and the dyeing step by the disperse dye alone were carried out, which was made Comparative Example 9. That is, Comparative Example 9 gives a material in which the mixed spinning aramid fabrics carried out the sulfuric acid treatment were dyed by the disperse dye alone. In this Comparative Example 9, the conditions of the sulfuric acid treatment and the dyeing by the disperse dye are the same as those of the above-mentioned Example 11.

**[0166]** The dyed mixed spinning aramid fabrics of Example 11, Comparative Example 8 and Comparative Example 9 which had been dyed as mentioned above were evaluated in the same manner as in the above-mentioned Example 1. However, lightness (L* value) was not measured. The evaluation results of the total K/S value which evaluates the color depth and colorfastness to light are shown in Table 11.

<table>
<thead>
<tr>
<th>Dye</th>
<th>Color depth (Total K/S value)</th>
<th>Lightness (L* value)</th>
<th>Colorfastness to light (grade)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Example 11 Vat + Disperse</td>
<td>153</td>
<td>—</td>
<td>3-4</td>
</tr>
<tr>
<td>Comparative example 8 Disperse</td>
<td>26</td>
<td>—</td>
<td>1-2</td>
</tr>
<tr>
<td>Comparative example 9 Disperse</td>
<td>136</td>
<td>—</td>
<td>2-3</td>
</tr>
</tbody>
</table>

**[0167]** As can be seen from Table 11, in Example 11, mixed spinning aramid fabrics markedly improved in color depth (total K/S value) and having a very dark color can be obtained. Also, the mixed spinning aramid fabrics of Example 11 have good colorfastness to light. Also, in the mixed spinning aramid fabrics of this Example 11, fuzz at the surfaces of the fabrics have been dyed by both of the vat dye and the disperse dye to a very dark color, and surface quality of the fabrics has been more improved. Further, whereas it is not shown in Table 11, in the dyed mixed spinning aramid fabrics of Example 11, the fabrics had maintained the practical properties of high performance fibers without generating color unevenness or dimensional change, or lowering in physical properties markedly. On the other hand, in Comparative Example 8, as compared with Example 11, color depth is inferior to that of Example, and colorfastness to light is markedly inferior to the same whereby no practically dyed product can be obtained. Also, in Comparative Example 9, whereas a sufficient color depth can be obtained, it is dyed only by the disperse dye so that colorfastness to light is markedly inferior to the same, and no practically dyed product can be obtained.
Example 12

[0168] In this Example 12, aramid fabrics were dyed based on the above-mentioned first embodiment and benzyl alcohol was used as a polar solvent. In Example 12, the same para-type aramid fabrics as those used in the above-mentioned Example 1 were used. The para-type aramid fabrics were used after desizing and degumming by the ordinary method.

A. Dye Providing Step

[0169] In this Example 12, the following vat dye was provided by the same operations as in the above-mentioned Example 1. A pickup ratio at this time was 58% by weight. As the dyeing solution, 50 g/L of the same vat dye “Mikethren Grey M super-fine” as in the above-mentioned Example 11 was dispersed in an unreduced state, and 10 g/L of GERMADEY AM-X (available from RAON CHEMICAL LTD.) was used as a migration preventive agent in combination.

[0170] Drying was carried out in the same steps of the above-mentioned Example 1, and the para-type aramid fabrics after providing the dyeing solution was dried at 110°C for 2 minutes to adhere the vat dye onto the surfaces of the fibers of the para-type aramid fabrics. The mixed spinning aramid fabrics after drying was injected into the subsequent solvent treatment step (benzyl alcohol treatment step) as such without carrying out washing or reduction washing.

B. Solvent Treatment Step (Benzyl Alcohol Treatment Step)

[0171] In this Example 12, benzyl alcohol (99.5% product) was used as a polar solvent without dilution. For providing the treating solution, a mangle device for testing was used, and the para-type aramid fabrics after the dyeing providing step were subjected to the solvent treatment by a continuous method. The treatment temperature at this time was 20°C. The treatment was carried out by immersing the para-type aramid fabrics into the treating solution for 1 second, and immediately squeezed by the mangle. A pickup ratio at this time was 61% by weight. Incidentally, in this Example 12, without carrying out the heat treatment after the solvent treatment, the para-type aramid fabrics after the solvent treatment step were washed with hot water and washed with water to remove the remaining benzyl alcohol, and then, reduction washing was carried out. The reduction washing was carried out in the same manner as in the above-mentioned Example 1. Thereafter, washing with hot water and washing with water were carried out and the fabrics were dried to obtain para-type aramid fabrics of Example 12 dyed to black having a practical color depth.

[0172] The dyed para-type aramid fabrics of Example 12 which had been dyed as mentioned above were evaluated in the same manner as in the above-mentioned Example 1. The evaluation results of the total K/S value which evaluates the color depth, lightness (L* value) which evaluates the degree of a dark color and colorfastness to light are shown in Table 12.

<table>
<thead>
<tr>
<th>Solvent</th>
<th>Color depth (Total K/S value)</th>
<th>Lightness (L* value)</th>
<th>Colorfastness to light (grade)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Example 12</td>
<td>81.9</td>
<td>37.9</td>
<td>4</td>
</tr>
</tbody>
</table>

[0173] As can be seen from Table 12, in Example 12, the para-type aramid fabrics have a practical color depth (total K/S value) and lightness (L* value), and also have good colorfastness to light. Further, whereas it is not shown in Table 12, in the dyed para-type aramid fabrics of Example 12, the fabrics had maintained the practical properties of high performance fibers without generating color unevenness or dimensional change, or lowering in physical properties markedly.

Example 13

[0174] In this Example 13, aramid fabrics were dyed based on the above-mentioned first embodiment and benzyl alcohol was used as a polar solvent. In this Example 13, to the dyed para-type aramid fabrics obtained in the above-mentioned Example 12, the same dyeing operation as in the above-mentioned Example 12 was repeated with a plural number of times. More specifically, the above-mentioned Example 12 was made the dyeing operation once, and the dyeing operation in which the dye providing step and the solvent treatment step had been combined was further repeated to carry out a total of 2 times, a total of 3 times and a total of 4 times of the dyeing operations. However, the reduction washing was carried out at after the final dyeing operation alone.

[0175] The dyed para-type aramid fabrics of Example 13 which had been dyed as mentioned above were evaluated in the same manner as in the above-mentioned Example 1. The evaluation results of the total K/S value which evaluates the color depth, lightness (L* value) which evaluates the degree of a dark color and colorfastness to light are shown in Table 13.

<table>
<thead>
<tr>
<th>Solvent</th>
<th>Dyeing operation (times)</th>
<th>Color depth (Total K/S value)</th>
<th>Lightness (L* value)</th>
<th>Colorfastness to light (grade)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Example 13</td>
<td>1</td>
<td>81.9</td>
<td>37.9</td>
<td>4</td>
</tr>
<tr>
<td>Example 12</td>
<td>2</td>
<td>129.0</td>
<td>28.1</td>
<td>4</td>
</tr>
<tr>
<td>Example 13</td>
<td>3</td>
<td>162.0</td>
<td>25.1</td>
<td>4-5</td>
</tr>
<tr>
<td>Example 13</td>
<td>4</td>
<td>183.9</td>
<td>23.3</td>
<td>5</td>
</tr>
</tbody>
</table>

[0176] As can be seen from Table 13, in the para-type aramid fabrics, as compared with Example 12 in which the dyeing operation is once, in Example 13, as a number of the dyeing operation increases, the color depth (total K/S value) is markedly improved, lightness (L* value) becomes small as 30 or less, whereby the para-type aramid fabrics with a very dark color could be obtained. The para-type aramid fabrics with a very dark color have had good colorfastness to light as
shown in Table 13. Further, whereas it is not shown in Table 13, in the dyed para-type aramid fabrics of Example 13, the fabrics had maintained the practical properties of high performance fibers without generating color unevenness or dimensional change, or lowering in physical properties markedly.

Example 14

[0177] In this Example 14, aramid fabrics were dyed based on the above-mentioned second embodiment and 4 kinds of polar solvents, triethylene glycol, formic acid, DL-lactic acid and oxalic acid were used as a polar solvent, respectively. In this Example 14, the same para-type aramid fabrics as in the above-mentioned Example 1 were used. The para-type aramid fabrics were used after desizing and degumming by the ordinary method.

A. Dye Providing Step

[0178] In this Example 14, the vat dye “Mikethren Grey M super-fine” was used as in the above-mentioned Example 12, and the same operations as in the above-mentioned Example 12 were carried out. A pickup rate at this time was 58% by weight. Drying was carried out in the same manner as in the above-mentioned Example 12. The mixed spinning aramid fabrics after drying was injected into the subsequent solvent treatment step as such without carrying out washing or reduction washing.

B. Solvent Treatment Step

[0179] In this Example 14, triethylene glycol (95% product), formic acid (98% product) and DL-lactic acid (85% product) were each used without dilution. On the other hand, oxalic acid (dihydrate) was dissolved in water and used as a 10% by weight aqueous solution. For providing the treating solution, a mangle device for testing was used, and the para-type aramid fabrics after the dye providing step were subjected to the solvent treatment by a continuous method. The treatment temperature at this time was each 20°C. The treatment was carried out by immersing the para-type aramid fabrics in the treating solution for 1 second and then immediately squeezed by the mangle. The pickup rates of the respective polar solvents at this time were 75% by weight for triethylene glycol, 71% by weight for formic acid, 81% by weight for DL-lactic acid, and 75% by weight for an aqueous oxalic acid solution, respectively.

C. Heat Treatment Step

[0180] For the heat treatment, a baking box device for testing was used, and the dry heat treatment was carried out to the para-type aramid fabrics after the respective solvent treatments at 110°C for 2 minutes to adhere the vat dye to the para-type aramid fabrics. The para-type aramid fabrics after the heat treatment was washed with hot water and washed with water to remove the respective polar solvents, and dried.

[0181] Next, reduction washing of the dyed para-type aramid fabrics after the heat treatment step was carried out. The reduction washing was carried out in the same manner as in the above-mentioned Example 1. Thereafter, washing with hot water and washing with water were carried out and the fabrics were dried to obtain para-type aramid fabrics of Example 14 dyed to black having a practical color depth.

[0182] The dyed para-type aramid fabrics of Example 14 which had been dyed as mentioned above were evaluated in the same manner as in the above-mentioned Example 1. The evaluation results of the total K/S value which evaluates the color depth, lightness (L* value) which evaluates the degree of a dark color and colorfastness to light are shown in Table 14.

<table>
<thead>
<tr>
<th>Dye Solvent</th>
<th>Color depth (Total K/S value)</th>
<th>Lightness (L* value)</th>
<th>Colorfastness to light (grade)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Example 14 Vat</td>
<td>Triethylene glycol</td>
<td>95.5</td>
<td>33.5</td>
</tr>
<tr>
<td></td>
<td>Formic acid</td>
<td>87.8</td>
<td>34.3</td>
</tr>
<tr>
<td></td>
<td>DL-lactic acid</td>
<td>97.1</td>
<td>32.7</td>
</tr>
<tr>
<td></td>
<td>Oxalic acid</td>
<td>75.5</td>
<td>37.3</td>
</tr>
</tbody>
</table>

[0183] As can be seen from Table 14, in Example 14, the para-type aramid fabrics have a practical color depth (total K/S value) and lightness (L* value) in either of 4 kinds of the polar solvents, and also have good colorfastness to light. Further, whereas it is not shown in Table 14, in the dyed para-type aramid fabrics of Example 14, the fabrics had maintained the practical properties of high performance fibers without generating color unevenness or dimensional change, or lowering in physical properties markedly.

Example 15

[0184] In this Example 15, aramid fabrics were dyed based on the above-mentioned third embodiment (pre-dyeing by disperse dye—dyeing by vat dye) and 5 kinds of the polar solvents, benzyl alcohol, triethylene glycol, formic acid, DL-lactic acid and oxalic acid were used as a polar solvent, respectively. In this Example 15, to the same para-type aramid fabrics as in the above-mentioned Example 1, a pre-dyeing step by a disperse dye was firstly carried out. Next, to the para-type aramid fabrics after the pre-dyeing step, the dyeing operation using the same vat dye and the respective polar solvents as in the above-mentioned Example 12 and Example 14 was carried out.

D1. Pre-Dyeing Step by Disperse Dye

[0185] Undyed para-type aramid fabrics were dyed by a disperse dye after desizing and degumming by the ordinary method. Dyeing was carried out by the immersion dyeing method, and the para-type aramid fabrics was dyed by using a high temperature and high pressure dyeing tester MINICOLOR (manufactured by TEXAM Giken Co., Ltd.). As the dyeing solution, 2.5% owf of Kayalon Polyester Black ECX-300 (disperse dye available from NIPPON KAYAKU Co., Ltd., C.I. No. unknown) and 2.5% owf of Kayalon Polyester Black IN-200 (C.I. No. unknown, disperse dye available from NIPPON KAYAKU Co., Ltd.) were used in combination, and an acetic acid/sodium acetate series buffer with pH 5 was used.

[0186] As a dyeing method, a high temperature and high pressure dyeing was carried out by making a bath ratio of 1:20, and under the conditions at 135°C for 60 minutes. Reduction washing was carried out to the para-type aramid
fabrics after dyeing in the same manner as in the dyeing of ordinary polyester fibers by a disperse dye. The reduction washing was carried out under the conditions of using 5 g/L of sodium dithionite as a reducing agent in combination with 5 g/L of sodium hydroxide at 80°C for 1 minute, and in this Example 15, reduction washing was repeated twice. Thereafter, washing with hot water and washing with water were carried out and the fabrics were dried to obtain para-type aramid fabrics which had been carried out the pre-dyeing by the disperse dye.

[0187] Next, the dyeing operations each of which uses benzyl alcohol, triethylene glycol, formic acid, DL-lactic acid or oxalic acid as a polar solvent, and the reduction washing were carried out to the para-type aramid fabrics carried out the pre-dyeing in the same manner as in the above-mentioned Example 12 or the above-mentioned Example 14 to obtain para-type aramid fabrics of Example 15 dyed to black which is a very dark color.

[0188] The dyed para-type aramid fabrics of Example 15 which had been dyed as mentioned above were evaluated in the same manner as in the above-mentioned Example 1. The evaluation results of the total K/S value which evaluates the color depth, lightness (L* value) which evaluates the degree of a dark color and colorfastness to light are shown in Table 15.

<table>
<thead>
<tr>
<th>TABLE 15</th>
</tr>
</thead>
<tbody>
<tr>
<td>&lt;&lt;para-type Aramid fabrics&gt;&gt;</td>
</tr>
<tr>
<td>Dye</td>
</tr>
<tr>
<td>------</td>
</tr>
<tr>
<td>Example 15</td>
</tr>
<tr>
<td></td>
</tr>
<tr>
<td></td>
</tr>
<tr>
<td></td>
</tr>
<tr>
<td></td>
</tr>
</tbody>
</table>

[0189] As can be seen from Table 15, as compared with the above-mentioned Example 12 (see Table 12) or the above-mentioned Example 14 (see Table 14) which had been dyed only by the vat dye, in Example 15 in which the pre-dyeing by the disperse dye has been carried out, dyeing densities (total K/S value) are markedly improved, and lightnesses (L* value) become smaller as 30 or less, and the para-type aramid fabrics with a very dark color can be obtained in the respective samples. The para-type aramid fabrics with a very dark color have extremely good colorfastness to light as shown in Table 15. Also, in the para-type aramid fabrics of this Example 15, fuzz at the surfaces of the fabrics have been dyed to a very dark color by both of the vat dye and the disperse dye, and the surface qualities of the fabrics has been improved. Further, whereas it is not shown in Table 15, in the dyed para-type aramid fabrics of Example 15, the fabrics had maintained the practical properties of high performance fibers without generating color unevenness or dimensional change, or lowering in physical properties markedly.

[0190] In this Example 16, aramid fabrics were dyed based on the above-mentioned third embodiment (pre-dyeing by cationic dye→dyeing by vat dye) and DL-lactic acid was used as a polar solvent. In this Example 16, to the same para-type aramid fabrics as in the above-mentioned Example 1, a pre-dyeing step by a cationic dye was firstly carried out. Next, to the para-type aramid fabrics after the pre-dyeing step, a dyeing operation by the same vat dye as in the above-mentioned Example 14 and by DL-lactic acid was carried out.

D1. Pre-Dyeing Step by Cationic Dye

[0191] Undyed para-type aramid fabrics were dyed by a cationic dye after desizing and degumming by the ordinary method. Dyeing was carried out by the immersion dyeing method, and the para-type aramid fabrics was dyed by using a high temperature and high pressure dyeing tester MINI-COLOR (manufactured by TExAM Giken Co., Ltd.). As the dyeing solution, 5.0% w/w of Kayacryl1 Navy RP-ED (Cl.No. unknown, cationic dye available from NIPPON KAYAKU Co., Ltd.) was used and 25 g/L of sodium nitrate and a commercially available dyeing carrier were also used in combination, and an acetic acid/sodium acetate series buffer with pH 5 was used.

[0192] As a dyeing method, a high temperature and high pressure dyeing was carried out by making a bath ratio of 1:20, and under the conditions at 135°C for 60 minutes. The para-type aramid fabrics after dyeing were carried out washing with hot water and washing with water, and dried to obtain para-type aramid fabrics which have been carried out a pre-dyeing by a cationic dye.

[0193] Next, to the para-type aramid fabrics which have been carried out the pre-drying, the dye providing step was carried out by using 50 g/L of the same vat dye “Mikethren Blue BC superfine” as in the above-mentioned Example 1 according to the same operations as in the above-mentioned Example 12. A pickup rate at this time was 58% by weight. Further, to the para-type aramid fabrics after the dye providing step, the solvent treatment step using DL-lactic acid as a polar solvent, the heat treatment step and the reduction washing were carried out in the same manner as in the above-mentioned Example 14 to obtain para-type aramid fabrics of Example 16 dyed to navy blue which is a very dark color.

Comparative Example 10

[0194] Similarly to the above-mentioned Example 16, dyeing by a cationic dye alone was carried out to the para-type aramid fabrics, which was made Comparative Example 10. More specifically, none of the dyeing operation of the dye providing step, the solvent treatment step and the heat treatment step according to the present invention was carried out, but the dyeing step by a cationic dye was carried out in the same manner as in the above-mentioned Example 16, thereafter, reduction washing, washing with hot water and washing with water were carried out to the fabrics in the same manner as in Example 16, and the fabrics were dried to obtain para-type aramid fabrics of Comparative Example 10 dyed to navy blue.

[0195] The dyed para-type aramid fabrics of Example 16 and Comparative Example 10 which had been dyed as mentioned above were evaluated in the same manner as in the above-mentioned Example 1. The evaluation results of the total K/S value which evaluates the color depth, lightness (L*
which evaluates the degree of a dark color and color-fastness to light are shown in Table 16.

### TABLE 16

<table>
<thead>
<tr>
<th>Solvent</th>
<th>Dye</th>
<th>Color depth</th>
<th>Lightness</th>
<th>Colorfastness to light</th>
<th>(grade)</th>
</tr>
</thead>
<tbody>
<tr>
<td>DL-lactic acid</td>
<td>Example 16 Cation+</td>
<td>137.8</td>
<td>26.3</td>
<td>3</td>
<td></td>
</tr>
<tr>
<td></td>
<td>Example 10 Cation</td>
<td>68.0</td>
<td>36.0</td>
<td>1</td>
<td></td>
</tr>
</tbody>
</table>

As can be seen from Table 16, in Example 16 dyed by the cationic dye and the vat dye, as compared with Comparative Example 10 dyed by the cationic dye alone, para-type aramid fabrics having a large color depth (total K/S value), and lightness (L* value) of as small as 30 or less, with a very dark color can be obtained. On the other hand, whereas colorfastness to light of Comparative Example 10 which has been dyed only by the cationic dye is remarkably weak, in Example 16 which has been dyed not only by the cationic dye but also by the vat dye, remarkable improvement in colorfastness to light can be recognized. Also, in the para-type aramid fabrics of this Example 16, fuzz at the surfaces of the fabrics have been dyed to a very dark color by both of the cationic dye and the vat dye, and surface quality of the fabrics has been more improved. Further, whereas it is not shown in Table 16, in the dyed para-type aramid fabrics of Example 16, the fabrics had maintained the practical properties of high performance fibers without generating color unevenness or dimensional change, or lowering in physical properties markedly.

As explained in the dyeing operations of the above-mentioned Example 1 to Example 16, according to the present invention, it can be applied to either of the para-type aramid fibers, the para-type copolymerized aramid fibers and the meta-type aramid fibers, and these aramid fibers can be dyed to a practical color depth. Also, according to the present invention, color unevenness or dimensional change, or lowering in physical properties is not markedly generated in the aramid fibers after the dyeing. Further, a vat dye or a sulfur dye having good colorfastness, in particular, good colorfastness to light is used so that colorfastness, in particular, colorfastness to light of the dyed aramid fibers becomes good.

Also, by changing a used concentration and hue of the vat dye or the sulfur dye to be used, dyed products with various hues from a pale color to a dark color can be obtained. In particular, according to the present invention, para-type aramid fibers or para-type copolymerized aramid fibers can be dyed to a very dark color (for example, L* value is 30 or less) such as black and navy blue which has been considered to be difficult as of today.

Further, as a pre- or post-step of the method for dyeing aramid fibers according to the present invention, by carrying out the pre-dyeing step or the post-dyeing step using a dye other than the vat dye and the sulfur dye, fuzz at the surface of the aramid fibers themselves are sufficiently dyed, dyeing quality becomes good, and further the color depth is improved. On the other hand, when the aramid fibers constitute mixed fibers with the other chemical fibers or natural fibers, by carrying out these dyeing steps, hue of the aramid fibers and that of the other fibers can be unified, whereby the dyeing quality and the color depth of the dyed product are further improved.

Therefore, according to the present invention, a method for dyeing aramid fibers and dyed aramid fibers in which colorfastness, in particular, colorfastness to light of the dyed product is good, hue thereof is abundant and the product has a practical color depth can be provided. This is effective for new applications of the aramid fibers.

Incidentally, for practicing the present invention, it is not limited by the above-mentioned respective Examples, the following various modified examples may be mentioned.

1. In the above-mentioned respective Examples, the solvent treatment step is carried out after the dye providing step, but the embodiment is not limited thereto, and the dye providing step may be carried out after the solvent treatment step.

2. In the above-mentioned respective Examples, after providing the dyeing solution containing the vat dye or the sulfur dye to the aramid fabrics, the said aramid fabrics are dried, but the embodiment is not limited thereto, and after providing the dyeing solution, the aramid fabrics may be injected into the solvent treatment step without drying.

3. In the above-mentioned respective Examples, whereas navy blue or black are used in many cases except for a part of vivid hue, these Examples are merely to show that fabrics can be dyed to a dark color or very dark color. Accordingly, by changing a used concentration and hue of the vat dye or the sulfur dye to be used, a dyed product from a pale color to a dark color with various hues including vivid hue can be obtained.

4. In the above-mentioned respective Examples, the aramid fibers to which the vat dye or the sulfur dye has been added in the dye providing step was injected into the subsequent solvent treatment step without washing. However, the vat dye or the sulfur dye is adhered to the aramid fibers with a certain degree of affinity after the dye providing step. Accordingly, the aramid fibers after the dye providing step may be injected into the solvent treatment step after washing.

5. In the above-mentioned respective Examples, reduction washing is carried out after the dyeing operation in some cases, but the reduction washing may be carried out only in the case where it is required, and a prescription of the reduction washing is not limited only to an alkaline series, and a reduction washing may be carried out with an acidic series reduction prescription.

6. In the above-mentioned Example 14 and Example 15, DL-lactic acid in which optical isomers have been mixed was used as a polar solvent, but the embodiment is not limited thereto, and D-lactic acid or L-lactic acid may be used.

7. In the above-mentioned Example 5, Example 11 and Example 15, neither a dyeing carrier nor a deep coloring agent is used for dyeing by a disperse dye. In the present invention, the pre-dyeing or the post-dyeing is merely auxiliary dyeing, and a dyeing carrier, etc., may not be used. However, by using various kinds of dyeing carriers, etc., used in the ordinary aramid dyeing in combination, the fabrics may be dyed to a darker color.

8. In the above-mentioned respective Examples, dyeing was carried out on the aramid fabrics, but the embodiment is not limited thereto, and it may be knitted fabrics, nonwoven fabrics, etc., or may be yarn, cotton, etc.

A method for dyeing aramid fibers which comprises a dye providing step in which a vat dye or a sulfur dye is
provided to aramid fibers, a solvent treatment step in which the aramid fibers are treated by a treating solution containing a polar solvent, and

after the solvent treatment step, a heat treatment step in which the aramid fibers are subjected to a heat treatment, if necessary, and having at least one dyeing operation among the following four dyeing operations,

dyeing operation 1: dye providing step followed by solvent treatment step,

dyeing operation 2: solvent treatment step followed by dye providing step,

dyeing operation 3: dye providing step followed by solvent treatment step followed by heat treatment step,

dyeing operation 4: solvent treatment step followed by heat treatment step followed by dye providing step, once or more.

2. The method for dyeing aramid fibers according to claim 1, wherein the polar solvent has a value of a solubility parameter (δ) within the range of 18 to 32 (MPa)^1/2.

3. The method for dyeing aramid fibers according to claim 1, wherein the polar solvent is at least one selected from the group consisting of N-methylpyrrolidone, N,N-dimethylformamide, N,N-dimethylacetamide, dimethylsulfoxide, benzyl alcohol, diethylene glycol, triethylene glycol, sulfuric acid, formic acid, lactic acid and oxalic acid.

4. A method for dyeing aramid fibers which comprises the method for dyeing aramid fibers according to claim 1, and a pre-dyeing step which is carried out before the method for dyeing or a post-dyeing step which is carried out after the same,

wherein the aramid fibers are dyed by a dye other than the vat dye and the sulfur dye in the pre-dyeing step or in the post-dyeing step.

5. Dyed aramid fibers which are dyed by the method for dyeing aramid fibers according to claim 1.

6. The dyed aramid fibers according to claim 5, wherein lightness (L* value) in an L*a*b* colorimetric system thereof is 38 or less.

7. The dyed aramid fibers according to claim 5, wherein lightness (L* value) in an L*a*b* colorimetric system thereof is 30 or less.

8. Dyed aramid fibers which are dyed by the method for dyeing aramid fibers according to claim 4.

9. The dyed aramid fibers according to claim 8, wherein lightness (L* value) in an L*a*b* colorimetric system thereof is 30 or less.

* * * * *